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Chemical Bonding

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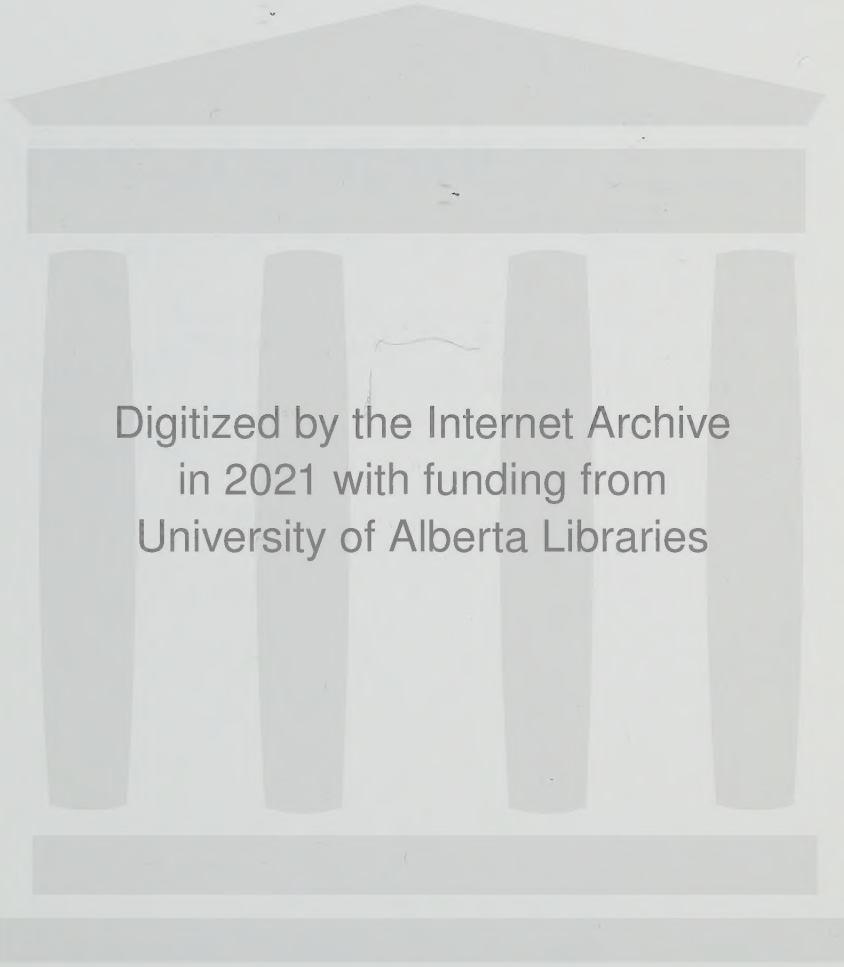


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NATIONAL SCIENCE CURRICULUM MATERIALS



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Chemical Bonding

R. D. Harcourt

*Department of Chemistry
University of Melbourne*

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The Jacaranda Press

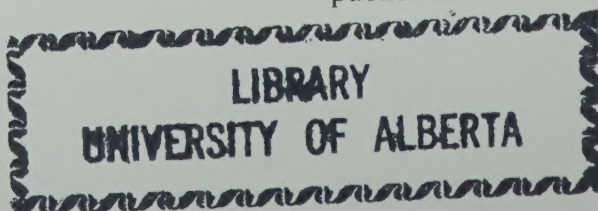
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PERIODIC TABLE

² He 4.00					
¹⁰ Ne 20.2	⁹ F 19.0	⁸ O 16.00	⁷ N 14.01	⁶ C 12.01	⁵ B 10.8
¹⁸ Ar 39.9	¹⁷ Cl 35.5	¹⁶ S 32.1	¹⁵ P 31.0	¹⁴ Si 28.1	¹³ Al 27.0

³ Li 6.94	⁴ Be 9.01
¹¹ Na 23.0	¹² Mg 24.3
¹⁹ K 39.1	²⁰ Ca 40.1
³⁷ Rb 85.5	³⁸ Sr 87.6
⁵⁵ Cs 132.9	⁵⁶ Ba 137.3
⁸⁷ Fr (223)	⁸⁸ Ra (226)

²¹ Sc 45.0	²² Ti 47.9	²³ V 50.9	²⁴ Cr 52.0	²⁵ Mn 54.9	²⁶ Fe 55.8
³⁹ Y 88.9	⁴⁰ Zr 91.2	⁴¹ Nb 92.9	⁴² Mo 95.9	⁴³ Tc (99)	⁴⁴ Ru 101.1
⁵⁷⁻⁷¹ La-Lu	⁷² Hf 178.5	⁷³ Ta 180.9	⁷⁴ W 183.9	⁷⁵ Re 186.2	⁷⁶ Os 190.2
⁸⁹⁻¹⁰³ Ac-Lw	¹⁰⁴	¹⁰⁵			

³¹ Ga 69.7	³⁰ Zn 65.4	²⁹ Cu 63.5	²⁸ Ni 58.7	²⁷ Co 58.9	²⁶ Fe 55.8
⁴⁹ In 114.8	⁴⁸ Cd 112.4	⁴⁷ Ag 107.9	⁴⁶ Pd 106.4	⁴⁵ Rh 102.9	⁴⁴ Ru 101.1
⁸¹ Tl 204.4	⁸⁰ Hg 200.6	⁷⁹ Au 197.0	⁷⁸ Pt 195.1	⁷⁷ Ir 192.2	⁷⁶ Os 190.2

⁵⁷ La 138.9	⁵⁸ Ce 140.1	⁵⁹ Pr 140.9	⁶⁰ Nd 144.2	⁶¹ Pm (145)	⁶² Sm 150.4	⁶³ Eu 152.0	⁶⁴ Gd 157.2	⁶⁵ Tb 158.9	⁶⁶ Dy 162.5	⁶⁷ Ho 164.9	⁶⁸ Er 167.3	⁶⁹ Tm 168.9	⁷⁰ Yb 173.0	⁷¹ Lu 175.0
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⁸⁹ Ac (227)	⁹⁰ Th 232.0	⁹¹ Pa (231)	⁹² U 238.0	⁹³ Np (237)	⁹⁴ Pu (242)	⁹⁵ Am (243)	⁹⁶ Cm (248)	⁹⁷ Bk (247)	⁹⁸ Cf (249)	⁹⁹ Es (254)	¹⁰⁰ Fm (253)	¹⁰¹ Md (256)	¹⁰² No (254)	¹⁰³ Lw (257)
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Parentnetical values are mass numbers of the isotopes with longest half lives

INTERNATIONAL ATOMIC WEIGHTS

(Atomic Weights relative to $^{12}\text{C} = 12$ exactly)

Atomic Number	Name	Symbol	Atomic Weight	Atomic Number	Name	Symbol	Atomic Weight
1	Hydrogen	H	1.008	31	Gallium	Ga	69.72
2	Helium	He	4.003	32	Germanium	Ge	72.59
3	Lithium	Li	6.939	33	Arsenic	As	74.92
4	Beryllium	Be	9.012	34	Selenium	Se	78.96
5	Boron	B	10.81	35	Bromine	Br	79.91
6	Carbon	C	12.01	36	Krypton	Kr	83.80
7	Nitrogen	N	14.01	37	Rubidium	Rb	85.47
8	Oxygen	O	16.00	38	Strontium	Sr	87.62
9	Fluorine	F	19.00	39	Yttrium	Y	88.91
10	Neon	Ne	20.18	40	Zirconium	Zr	91.22
11	Sodium	Na	22.99	41	Niobium	Nb	92.91
12	Magnesium	Mg	24.31	42	Molybdenum	Mo	95.94
13	Aluminium	Al	26.98	43	Technetium*	Tc	(99)
14	Silicon	Si	28.09	44	Ruthenium	Ru	101.1
15	Phosphorus	P	30.97	45	Rhodium	Rh	102.9
16	Sulphur	S	32.06	46	Palladium	Pd	106.4
17	Chlorine	Cl	35.45	47	Silver	Ag	107.9
18	Argon	Ar	39.95	48	Cadmium	Cd	112.4
19	Potassium	K	39.10	49	Indium	In	114.8
20	Calcium	Ca	40.08	50	Tin	Sn	118.7
21	Scandium	Sc	44.96	51	Antimony	Sb	121.8
22	Titanium	Ti	47.90	52	Tellurium	Te	127.6
23	Vanadium	V	50.94	53	Iodine	I	126.9
24	Chromium	Cr	52.00	54	Xenon	Xe	131.3
25	Manganese	Mn	54.94	55	Caesium	Cs	132.9
26	Iron	Fe	55.85	56	Barium	Ba	137.3
27	Cobalt	Co	58.93	57	Lanthanum	La	138.9
28	Nickel	Ni	58.71	58	Cerium	Ce	140.1
29	Copper	Cu	63.54	59	Praseodymium	Pr	140.9
30	Zinc	Zn	65.37	60	Neodymium	Nd	144.2

*Unstable elements

Parenthetical numbers refer to the mass number (not the atomic weight) of the isotope with the longest half-life.

INTERNATIONAL ATOMIC WEIGHTS

(Atomic Weights relative to $^{12}\text{C} = 12$ exactly)

Atomic Number	Name	Symbol	Atomic Weight	Atomic Number	Name	Symbol	Atomic Weight
61	Promethium*	Pm	(145)	86	Radon*	Rn	(222)
62	Samarium	Sm	150.4	87	Francium*	Fr	(223)
63	Europium	Eu	152.0	88	Radium*	Ra	(226)
64	Gadolinium	Gd	157.3	89	Actinium*	Ac	(227)
65	Terbium	Tb	158.9	90	Thorium*	Th	232.0
66	Dysprosium	Dy	162.5	91	Protactinium*	Pa	(231)
67	Holmium	Ho	164.9	92	Uranium*	U	238.0
68	Erbium	Er	167.3	93	Neptunium*	Np	(237)
69	Thulium	Tm	168.9	94	Plutonium*	Pu	(242)
70	Ytterbium	Yb	173.0	95	Americium*	Am	(243)
71	Lutetium	Lu	175.0	96	Curium*	Cm	(248)
72	Hafnium	Hf	178.5	97	Berkelium*	Bk	(247)
73	Tantalum	Ta	180.9	98	Californium*	Cf	(249)
74	Tungsten	W	183.9	99	Einsteinium*	Es	(254)
75	Rhenium	Re	186.2	100	Fermium*	Fm	(253)
76	Osmium	Os	190.2	101	Mendelevium*	Md	(256)
77	Iridium	Ir	192.2	102	Nobelium*	No	(254)
78	Platinum	Pt	195.1	103	Lawrencium*	Lw	(257)
79	Gold	Au	197.0	104	(Kurchatovium)		
80	Mercury	Hg	200.6				
81	Thallium	Tl	204.4				
82	Lead	Pb	207.2				
83	Bismuth	Bi	209.0				
84	Polonium*	Po	(210)				
85	Astatine*	At	(210)				

*Unstable elements

Parenthetical numbers refer to the mass number (not the atomic weight) of the isotope with the longest half-life.

After studying this topic you should know:

- the history of the concept of a valence structure;
- the stabilities of the electron configurations for the noble gases, and their relevance to the Lewis theory of chemical bonding;
- the formation of covalent bonds by sharing the unpaired electrons of two or more atoms;
- the construction of Lewis valence formulas with electron-pair covalent bonds;
- differences between covalent and ionic bonds;
- the prediction of molecular shapes; and
- theories concerning the origin of the binding energy for the hydrogen molecule.

You should be able to:

- write down Lewis valence formulas for molecules;
- decide when ionic bonding might be appropriate;
- predict the polarities of bonds; and
- predict the shapes of many triatomic and polyatomic molecules.

Some History Before 1916

We shall begin our account of chemical bonding by describing very briefly some historical aspects prior to 1916. In that year the American chemist G. N. Lewis (1875-1946) and the German physicist W. Kossel (1888-1956), proposed theories of bonding which form the basis of our ideas today, and with which we shall be largely concerned in this booklet.

The English chemist John Dalton (1766-1844), used the symbol $\odot$ to represent an atom of the element hydrogen; $\bigcirc$ to represent an atom of the element oxygen; and $\oplus$ to represent an atom of the element nitrogen.

With these symbols he wrote the following formulas for atoms:

water $\odot \bigcirc$
ammonia $\odot \oplus$
nitrous oxide $\bigcirc \oplus$.

In 1814, the Swedish chemist J. J. Berzelius (1779-1848) had introduced chemical symbols, most of which we still use today. For water Berzelius wrote $2\text{H} + \text{O}$, which indicates the chemical combination of two volumes of hydrogen with one volume of oxygen. He represented cuprous oxide as $\text{Cu} + \text{O}$; sulphuric acid as $\text{S} + 3\text{O}$; and copper sulphate as $\text{CuO} + \text{SO}^3$, in which the number of oxygen atoms in the sulphate part is indicated by the superscript 3.

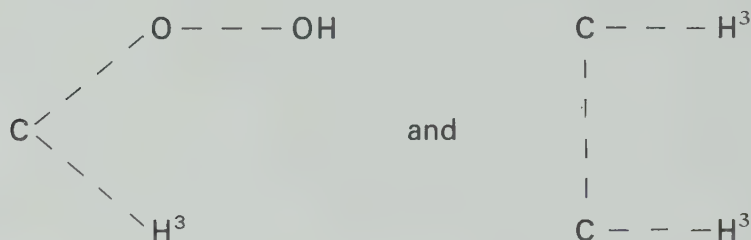
To the English chemist Sir Edward Frankland (1825-1899), goes the credit of stating in 1852, that atoms have a definite **combining power**.

For example a phosphorus atom can combine with three atoms of hydrogen, to form phosphine PH_3 . The combining power of phosphorus is three and that of hydrogen is one. One phosphorus atom can also combine with five atoms of chlorine to form phosphorus pentachloride, PCl_5 . The combining power of phosphorus is five and that of chlorine is one. Frankland recognized the possibility of variable combining powers for many types of atoms.

In 1858 a combining power of four for the carbon atom was suggested independently by the German chemist F. A. Kekulé (1829-1896), and the Scottish chemist A. S. Couper (1831-1892).

Couper introduced lines to link atoms or radicals in the graphical (or structural) formulas.

For methanol (CH_3OH) and ethane (C_2H_6), he wrote the structural formulas:



in which he used the symbol $\text{O} - - - \text{O}$ for the oxygen atom. (Couper assumed that the atomic weight of oxygen was 8.)

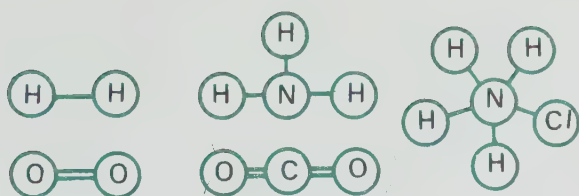
Couper published his papers in both English and French. To represent the atomic links, he used broken ($- - -$) and full ($—$) lines respectively, in the English and French papers. The full lines are used by chemists today and are called **valence bonds**. Couper indicated that these bond lines signify the degree of combining power, i.e. the **valence** of the atoms. The German chemist H. Wichelhaus, introduced the term 'valence' in 1868. The word valence is derived from the Latin *valentia* which means capacity, or strength.

It is of interest to note, that in 1789, the English chemist William Higgins (1762-1825), had used bond lines to connect atoms in some chemical diagrams.

The term **chemical structure** was first used by the Russian chemist A. M. Butlerov (1826-1886), in 1861. He realized that structural formulas could be written for every compound and that each structural formula represents one compound.

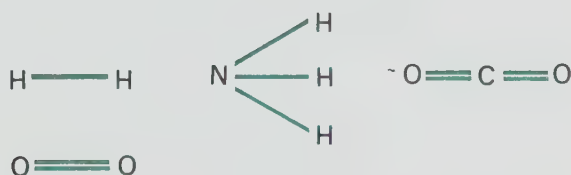
In the 1860s, several books making use of Couper's valence theory were published. In 1886, Frankland published *Lecture Notes for Students of Chemistry* and used true atomic weights ($\text{C} = 12$, $\text{O} = 16$), as well as the notation of valence bonds.

For molecules of hydrogen, oxygen, ammonia, carbon dioxide and ammonium chloride, he wrote the following structural or **valence** formulas:



The structural formulas indicate a valence of one for hydrogen, two for oxygen, four for carbon, one for chlorine and both three and five for nitrogen.

Other chemists were omitting the circles around the atomic symbols, and valence formulas for H_2 , O_2 , NH_3 and CO_2 were written as:



which are similar to those we use today.

In 1874, the Dutch chemist J. H. van't Hoff (1852-1911), and the French chemist J. A. Le Bel (1847-1930), independently suggested that valence bonds could have directional properties, and that the four valence bonds of a saturated carbon atom (as in CH_4) pointed towards the corners of a tetrahedron. Therefore, the valence formulas can represent the three-dimensional arrangements of atoms in a molecule.

In this booklet, we shall be concerned with understanding the nature of the chemical bonds between atoms in molecules, and also with how the type of bond can determine the properties of a molecule. For chemists of the nineteenth century, the nature of the chemical bonds was not understood satisfactorily. In 1807, the English chemist Sir Humphry Davy (1778-1829), on the basis of his electrolysis experiments, suggested that all matter consisted of electrically charged bodies, and that chemical union came about by neutralization of the positive charge on one body with the negative charge on another body. Berzelius, in 1831, developed this idea further on an atomic basis. Both positive and negative electricity were assumed to be present in any atom, but the atoms of most elements were assumed to possess more of one type of electricity than of the other. This dualistic theory is essentially

correct for salt-type compounds such as sodium chloride, but it is not satisfactory for molecules such as hydrogen (H_2) and methane (CH_4). In dilute aqueous solution, sodium chloride separates into sodium ions ($\text{Na}_{(aq)}^+$), and chloride ions ($\text{Cl}_{(aq)}^-$). Fused sodium chloride is an electrical conductor. This and other evidence suggests that a molecule of sodium chloride consists essentially of ions in combination. On the other hand, molecules such as hydrogen and methane, do not form ionic solutions, and there is no evidence to suggest that these molecules are ionic. To the nineteenth century chemists, it seemed that there were two types of chemical bonds. In 1916, Lewis suggested that the bonds of H_2 and NaCl represent two extreme types of chemical bonding, (namely **covalent bonds** and **ionic bonds**). However, as we shall show in this booklet, all gradations between these two extremes are possible.

With the discovery of the electron in 1897, by the English physicist J. J. Thomson (1856-1940), many chemists quickly realized that chemical bonding somehow involved electrons. By 1916, the concept of **atomic number** had been established through the work of the New Zealand physicist Lord Rutherford (1871-1937) and the English physicist, Henry Moseley (1887-1915). The atomic number of an atom is equal to its nuclear charge, and since atoms are electrically neutral, *the atomic number must be equivalent to the number of electrons present in the atom.*

In 1916, G. N. Lewis and Walter Kossel independently published papers which described electronic theories of chemical bonding. They pointed out that atoms of the noble gases, helium, neon and argon, must have particularly stable arrangements of electrons, because these elements were not known to form chemical compounds. Lewis and Kossel also suggested that atoms of other elements could also become more stable, by acquiring the electronic configurations of noble gases. As we shall find in the following sections of this booklet, there are two ways in which atoms acquire such configurations; either by **electron transfer**, or by **electron sharing**.

The bonding which arises from electron transfer is called **ionic bonding**, and that arising from electron sharing is called **covalent bonding**.

To understand these electronic theories of chemical bonding, it is necessary to know the electronic structures of atoms. We could describe these theories using the atomic theories of Lewis and Kossel, but this would complicate matters. It is more usual to use the atomic orbital theory which was developed after 1926. The term **orbital** was first suggested by the American chemist R. S. Mulliken in 1932.

Summary of the Orbital Theory

The electronic configurations of atoms are discussed in the NSCM Booklets C1, The Chemist’s View of the Atom, and C6, Chemical Periodicity—Part 1, and we shall only summarize the relevant aspects here.

Electrons in atoms are assumed to occupy atomic orbitals; not more than two electrons may occupy any orbital simultaneously.

Table 1. Electron configurations, atomic numbers and ionization energies (kJ mol⁻¹)

Element (A)	Z	1s	2s	2p	3s	3p
H 1s ¹	1	1313				
He 1s ²	2	2380				
Li 1s ² 2s ¹	3	6260	525			
Be 1s ² 2s ²	4	11700	906			
B 1s ² 2s ² 2p ¹	5	19000	1350	551		
C 1s ² 2s ² 2p ²	6	28400	1880	1040		
N 1s ² 2s ² 2p ³	7	39400	2470	1250		
O 1s ² 2s ² 2p ⁴	8	52400	3120	1540		
F 1s ² 2s ² 2p ⁵	9	67200	3870	1800		
Ne 1s ² 2s ² 2p ⁶	10	84000	4670	2090		
Na 1s ² 2s ² 2p ⁶ 3s ¹	11	104000	6830	3680	499	
Mg 1s ² 2s ² 2p ⁶ 3s ²	12	127000	9190	5380	735	
Al 1s ² 2s ² 2p ⁶ 3s ² 3p ¹	13	151000	11800	7610	1090	578
Si 1s ² 2s ² 2p ⁶ 3s ² 3p ²	14	178000	15100	10200	1440	748
P 1s ² 2s ² 2p ⁶ 3s ² 3p ³	15	208000	18500	13300	1770	945
S 1s ² 2s ² 2p ⁶ 3s ² 3p ⁴	16	239000	22300	16400	2020	1130
Cl 1s ² 2s ² 2p ⁶ 3s ² 3p ⁵	17	274000	26600	20100	2440	1330
Ar 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶	18	310000	31800	24300	2820	1520

If an atomic orbital is singly occupied, the electron is said to be **unpaired**, but when two electrons occupy an atomic orbital, the electrons are said to be **paired**.

There are one $1s$, one $2s$, three $2p$, one $3s$ and three $3p$ atomic orbitals. These are the orbitals with which we shall be chiefly concerned. Later in the booklet, we shall also refer to the $3d$ orbitals, of which there are five.

Table 1 gives the following information about the first eighteen elements.

- the atomic number;
- the electronic configurations of the atoms;
- the ionization energies (kJ mol^{-1}) which represent the energies needed to remove a $1s$, $2s$, $2p$, $3s$ or $3p$ electron from the atom.

The symbol $\bigcirc$ is used to represent an empty orbital. An orbital with one electron is represented by $\bullet$ or by $\odot$. This is called a half-filled orbital. A filled orbital is represented by the symbol $\otimes$. This symbol means that there are two electrons in the orbital. The electronic configuration of atoms of boron, carbon, nitrogen, oxygen, fluorine and neon are shown in figure 1.

$1s^2$	$2s^2$	$2p^1$	boron
$\otimes$	$\otimes$	$\odot \bigcirc \bigcirc$	
$1s^2$	$2s^2$	$2p^2$	carbon
$\otimes$	$\otimes$	$\odot \odot \bigcirc$	
$1s^2$	$2s^2$	$2p^3$	nitrogen
$\otimes$	$\otimes$	$\odot \odot \odot$	
$1s^2$	$2s^2$	$2p^4$	oxygen
$\otimes$	$\otimes$	$\otimes \odot \odot$	
$1s^2$	$2s^2$	$2p^5$	fluorine
$\otimes$	$\otimes$	$\otimes \otimes \odot$	
$1s^2$	$2s^2$	$2p^6$	neon
$\otimes$	$\otimes$	$\otimes \otimes \otimes$	

Figure 1. Electron configurations for ground states B, C, N, O, F and Ne atoms

Diatomic Molecules and Ions formed from Hydrogen and Helium Atoms

We shall study the bonding and valence formulas for the simplest diatomic molecule and ions, namely the hydrogen molecule H_2 , the hydrogen molecule ion H_2^+ , and the helium molecule ion He_2^+ , which are formed from hydrogen and helium atoms or ions. A study of these systems forms the basis for understanding the bonding which can occur between pairs of similar atoms in many other molecular systems. Such bonding is called **covalent bonding**.

The Hydrogen Molecule and the Electron-Pair Bond

Let us first examine the hydrogen and helium atoms. Their atomic numbers are 1 and 2, and therefore they have one and two electrons respectively. For the ground states, the electron configurations of these atoms are $1s^1$ and $1s^2$. These configurations indicate that a hydrogen atom has one *unpaired* electron, and that a helium atom has two *paired* electrons, (see figure 2).

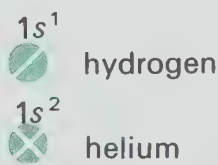
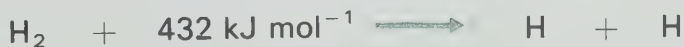


Figure 2. Electron configurations of H and He

Helium atoms do not react chemically with each other, and the molecule He_2 does not exist as a stable species. By contrast, the hydrogen molecule H_2 is physically stable—it has a **dissociation energy** of 432 kJ mol^{-1} , i.e. we need this amount of energy to ‘break up’ or dissociate the molecule into two hydrogen atoms.



This indicates that H_2 is more stable than two hydrogen atoms.

How may we account for the stability of the hydrogen molecule? In 1916, Lewis noted that the helium atom with two electrons is unreactive, and then suggested that a hydrogen atom could also

achieve stability by **sharing** or **pairing** its electron with the electron of another hydrogen atom. Therefore, according to Lewis, the valence bond of H_2 consists of a *pair of shared electrons*.

Lewis wrote:



as the valence formula. The two dots represent a pair of electrons, and each chemical symbol H represents the atomic nucleus of a hydrogen atom (i.e., a proton, H^+).

This suggestion of Lewis, namely that the valence bond of H_2 consists of a pair of shared electrons, was acknowledged in 1964 by the English chemist J. W. Linnett, as 'probably the most important and productive contribution that has ever been made to

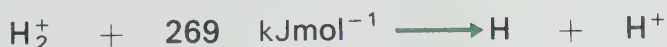


Figure 3. John Wilfred Linnett, the British chemist and lecturer, was born in Coventry in 1913 and educated there at the King Henry VIII School, and later at Oxford and Harvard Universities. He has a Ph.D. degree, and is a Fellow of the Royal Society. From 1939 to 1945, Dr Linnett held a Junior Research Fellowship at Balliol College, Oxford; he has been Professor of Physical Chemistry at Cambridge since 1965.

the subject of valence and chemical bonding.' As we shall find later, the bonds between a great many other pairs of atoms may also be described in terms of one or more pairs of shared electrons. In 1919, the American chemist I. Langmuir (1881-1957), gave the name of covalent bond to those chemical bonds which involve the mutual sharing of electrons by two atoms.

The Hydrogen Molecule Ion and the One-Electron Bond

Although **electron-pair** bonds are the usual types of covalent bonds, there are a number of molecular systems which have one-electron bonds. The simplest of these is the hydrogen molecule ion, H_2^+ . Since H_2 has two electrons, H_2^+ must have only one electron. H_2^+ is prepared by passing an electrical discharge through hydrogen gas. Because of the positive charge, H_2^+ is chemically very reactive. It can dissociate into a hydrogen atom and a proton. The dissociation energy is 269 kJ mol^{-1} :



The bond of H_2^+ is therefore weaker than the bond of H_2 . This is not surprising, as H_2^+ has only one electron available for bonding, whereas H_2 has two. We may write the valence formula for H_2^+ as:



thereby showing that one electron is equally shared by the two protons.

The Helium Molecule

We have already indicated that helium atoms, with two electrons, are chemically inert. The two electrons of a helium atom are paired with each other in the $1s$ atomic orbital, and therefore they may not be shared with the electrons of another helium atom. The 'reaction' between two helium atoms may be written as



rather than as



Thus no covalent bond is formed between the helium atoms.

The molecule He_2 does not exist as a stable species. For each helium atom, the pair of $1s$ electrons may be called **non-bonding** electrons.

The Helium Molecule Ion

Although He_2 does not exist as a stable molecule, the helium molecule ion, He_2^+ , has appreciable stability. The dissociation energy of this ion is 230 kJ mol^{-1} .



The dissociation products are He and He^+ . He has an electronic configuration, $1s^2$, with two paired electrons; He^+ has an electron configuration $1s$, with one unpaired electron, (see figure 4).

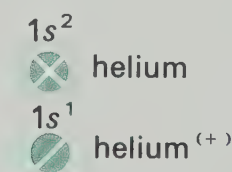
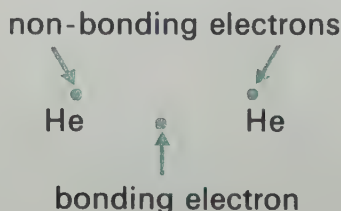


Figure 4. Electron configuration of He and He^+

Together, they have only one unpaired electron, and therefore we might assume that the chemical bond of He_2^+ involves the sharing of this electron. If this is true, then we are able to account for the similarity of the measured bond strengths of He_2^+ and H_2^+ (230 and 269 kJ mol^{-1} respectively)—both ions use only one electron for covalent bonding. For He_2^+ , the other two electrons are non-bonding electrons, i.e. electrons which are not shared to form a covalent bond.

A valence formula for He_2^+ , which shows one bonding and two non-bonding electrons is:



This valence formula was not deduced by Lewis. It was suggested first by another American chemist and Nobel Prize winner, Linus Pauling, in 1931. He wrote the valence formula as



and called the bond a ‘**three electron bond**’. More recently, Linnett, in 1964, recommended that we write the formula as we have done above, thereby emphasizing that one electron is responsible for bonding.

Pauling and Linnett have shown that valence formulas for NO, O₂, and NO₂, use the He₂⁺ distribution of electrons, i.e. two non-bonding and one bonding electron, for three of the electrons of each of these molecules. Except for O₂, this distribution has been restricted to molecules with an uneven number of electrons.

Recently, the author has shown how to incorporate the distribution into the valence formulas of many molecules with an even number of electrons. Later, we shall consider this topic in a little more detail. However, in much of this booklet, we shall concentrate on the electron-pair bonds of Lewis.

Bond Lengths

The experimental bond strengths (dissociation energies), have already been discussed. It is also possible to measure the distances between pairs of atomic nuclei in a molecule (or a molecular ion). To do this, diffraction and spectroscopic techniques are used, the details of which need not concern us here. The distances are called either interatomic distances, or internuclear distances, or **bond lengths**. We shall use the last term. Bond lengths are often expressed as multiples of a very small unit of length called the picometre, (pm), which is 10⁻¹² m.

Exercise

- 1 For H₂⁺, H₂, He₂⁺ and He₂, bond lengths have been measured. When mixed up, they are 74 pm, 106 pm, infinity and 108 pm. Sort them out, and then construct a table with the following headings: molecular system, valence formula, number of bonding electrons, bond length, and dissociation energy. When it is completed, your table should indicate that the number of bonding electrons is related to the lengths and strengths of the bonds. Can you predict the properties of the anion H₂⁻?

Elements of the Second Row in the Periodic Table

Table 1 gives the electronic configuration for atoms of the second row elements (Li, Be, B, C, N, O, F and Ne). For each of these atoms, the 1s atomic orbital is doubly occupied, just as it is for the helium atom. In the same table, we find that the ionization energies of the 1s electrons are very large, compared with those of the 2s and 2p electrons, indicating that the 1s electrons are very firmly bound. Therefore, they cannot be used easily for covalent bonding.

The 1s electrons are called **inner shell** electrons, and we shall omit all inner shell electrons from our bonding descriptions. The remaining electrons which occupy the 2s and 2p atomic orbitals are called **valence shell** electrons, or valence electrons.

We shall use these electrons to discuss the bonding for some diatomic molecules and ions involving second row atoms. To do so, it is necessary to write down valence formulas for the atoms. These are given in table 2, page 13, together with those for some isoelectronic ions. (Ions with the same number of electrons.) When two electrons occupy the same atomic orbital, thus forming a pair of non-bonding electrons, we have represented the electrons by two dots in the same region of space around the atomic symbol. The atomic symbols in these formulas represent the atomic nucleus, plus the inner shell electrons. Lewis gave the name of '**atomic kernel**' to the atomic nucleus plus inner shell electrons of an atom.

Exercise

- 2 For the Lewis theory of valence, can you explain why the valence of an atom or ion is equivalent to the number of unpaired electrons that pertains to the atom or ion?

Di-lithium Li_2

The lithium atom, with one valence electron, may share this electron with a second lithium atom to form the valence bond of the dilithium molecule, Li_2 . We may write:



The cation Li_2^+ is also known. Since Li has one electron and Li^+ has none, Li_2^+ has a one-electron bond. Its valence formula is therefore similar to that of H_2^+ , i.e. $\text{Li} \bullet \text{Li}$. On page 11, we have found that the one-electron bond of H_2^+ is longer than the two-electron bond of H_2 . Li_2^+ also has a longer bond than Li_2 . The length of the one-electron bond in Li_2^+ is 303 pm, while the length of the two-electron bond in Li_2 is 267 pm. Both H_2 and Li_2 have a *single bond*, which consists of a pair of shared electrons.

Table 2. Valence electron configurations and valence formulas for second-row atoms and isoelectronic ions

(a) Ground-state configurations and formulas

$2s^1$	$\text{Li} \bullet$	$2s^2$	$\text{Be} :$
$2s^2 2p^1$	$\bullet \text{B} :$	$2s^2 2p^2$	$\sim \bullet \text{C} : , \bullet \text{N} :^+ , \bullet \text{B} :^-$
$2s^2 2p^3$	$\bullet \text{N} : , \bullet \text{O} :^+$	$2s^2 2p^4$	$\bullet \text{O} :$
$2s^2 2p^5$	$\bullet \text{F} : , \bullet \text{O} :^-$	$2s^2 2p^6$	$:\text{Ne} : , :\text{F} :^- , :\text{O} :^{2-}$

(b) Promoted or excited configurations

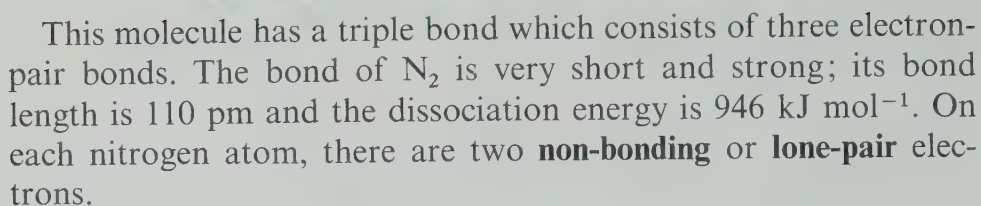
$2s^1 2p^1$	$\bullet \text{Be} \bullet$	$2s^1 2p^2$	$\bullet \text{B} \bullet$
$2s^1 2p^3$	$\bullet \text{C} \bullet , \bullet \text{N} \bullet^+ , \bullet \text{B} \bullet^-$		

'Di-beryllium' Be_2 , and 'Di-neon' Ne_2 .

The valence electron configurations of atoms of beryllium and neon are $2s^2$, and $2s^2 2p^6$, respectively. Since they have no unpaired electrons, it is easy to understand why Be_2 and Ne_2 do not exist as stable molecules.

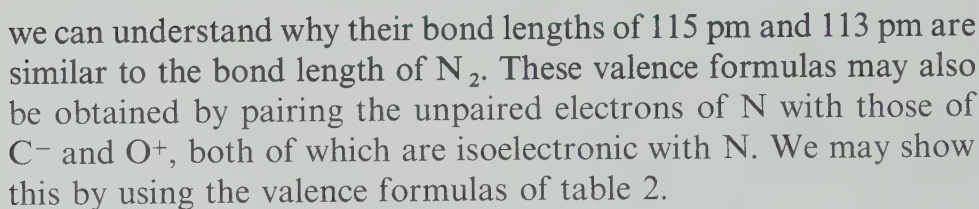
The Nitrogen Molecule

In table 2, we find that the nitrogen atom has three unpaired electrons occupying three $2p$ atomic orbitals. By pairing these with the unpaired electrons of another nitrogen atom, we may obtain the valence formula for the nitrogen molecule, N_2 .



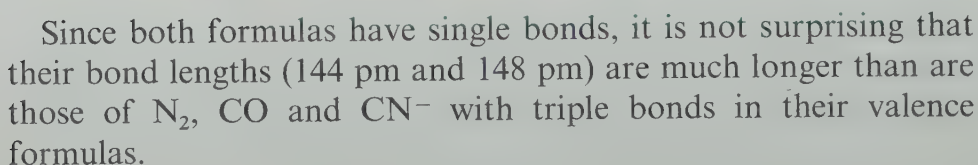
The nitrogen molecule has ten valence electrons, and it is isoelectronic with the cyanide anion CN^- , and with carbon monoxide, CO . (We may verify this statement by counting the electrons of each system.)

If we assume that CN^- and CO have valence formulas which are similar to that of N_2 , namely



The Fluorine Molecule and the Peroxide Ion

F and O^- are isoelectronic with $2s^2 2p^5$ configurations, and therefore have only one unpaired electron each. By using them, we may generate similar valence formulas for F_2 and O_2^{2-} .



Exercises

- 3 H_2 , Li_2 , F_2 , and O_2^{2-} , each has a single bond. However, their bond lengths vary considerably. Using atomic number and atomic orbital considerations, can you suggest some reasons to explain why the lengths are different?
- 4 For the atoms of the third row elements Na, Ar, write down the electron configurations of the inner shell electrons and the valence shell electrons. What are the kernels of these atoms? Deduce valence formulas for Na_2^+ , Na_2 , Cl_2 , Ar_2 , and PN . Which of these species should be unstable, and which should have the strongest bond?
- 5 The bond lengths of F_2 , Cl_2 , Br_2 and I_2 are found to be 144 pm, 198 pm, 228 pm and 266 pm, respectively. Write down valence formulas for these molecules, and try to explain why the bond lengths vary.

The Oxygen Molecule

The oxygen atom, with the $2s^2 2p^4$ valence electron configuration, has two unpaired electrons. By pairing these electrons with the two unpaired electrons of a second oxygen atom, we may obtain the Lewis valence formula for O_2 .



This valence formula has a **double bond**, which consists of two electron-pair bonds. We might therefore expect the bond length of O_2 to be intermediate between the triple bond length of N_2 and the single bond length of F_2 or O_2^{2-} . The measured length of 121 pm shows that this is the case.

Magnetic Properties of Molecules

If a molecule or ion is attracted by a magnetic field, it is **para-magnetic**; if it is repelled, it is **diamagnetic**. All molecules or ions with an uneven or odd number of electrons are paramagnetic, whereas nearly all molecules or ions with an even number of electrons are diamagnetic.

Since 'odd' molecules have at least one unpaired electron, and even' molecules have none, we might suspect that paramagnetism is related to the *presence of an unpaired electron*.

Exercise

- 6 Count up the number of electrons and the number of unpaired electrons that are present for H_2^+ , H_2 , He_2^+ , Li_2^+ , Li_2 , N_2 , O_2 , F_2 and O_2^{2-} , and then predict their magnetic properties.

If you have done this exercise, you have probably predicted O_2 to be diamagnetic, because the molecule has 16 electrons, and the Lewis formula indicates that there are no unpaired electrons. Your prediction is incorrect; O_2 is a paramagnetic molecule. Why did you go wrong? Probably because you assumed that the Lewis formula, with electron pair bonds and lone-pairs of electrons, was a satisfactory valence formula for O_2 . It obviously cannot be satisfactory—it has no unpaired electrons. Because of this Lewis suggested that the valence formula (a) in figure 5, with two unpaired electrons, was appropriate for O_2 . However, this is also unsatisfactory because it has a single bond, and therefore suggests that the bond lengths of O_2 and O_2^{2-} should be very similar. What then is a suitable valence formula which indicates that O_2 is paramagnetic and that it has a bond length which is much shorter than a single bond? It was left to Pauling, in 1931, to answer that question. He suggested that the O_2 valence formula was (b). In 1960, Linnett showed that this formula was better written as (c) and we shall use this in our discussion.

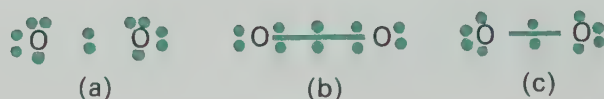


Figure 5. Various valence formulas for O_2

We may compare valence formula (c) with those which are shown earlier for H_2 and He_2^+ . Formula (c) has one electron-pair bond, as has H_2 , but it also has two sets of electrons which are arranged similarly to those of He_2^+ . Since He_2^+ is paramagnetic, these electrons, i.e. those of $\begin{array}{c} \text{O} \\ \cdot \end{array} \cdot \begin{array}{c} \text{O} \\ \cdot \end{array}$ and $\begin{array}{c} \text{O} \\ \cdot \end{array} \cdot \begin{array}{c} \text{O} \\ \cdot \end{array}$ must be responsible

for the paramagnetism of O_2 . Unlike (a), formula (c) has four bonding electrons due to the presence of an electron-pair bond and two one-electron bonds.

Nitric oxide, NO, has 11 valence electrons and is therefore paramagnetic. Linnett has written its valence formula as



This formula has five bonding electrons, and it is therefore compatible with the NO bond length of 115 pm being shorter than the 121 pm for O_2 .

Exercises

7 How many valence electrons do O_2 , S_2 , SO, NO and O_2^+ have? Write the valence formulas for these systems, and then predict their magnetic properties.

8 Starting with two oxygen atoms, with their electrons arranged



can you derive the valence formula for O_2 as in figure 5 (c) ?

Bond Polarity, Electronegativity, Ionic Bonding

Earlier, we discussed the bonding for diatomic molecules and ions which consist of two atoms having the same atomic number. We shall now examine the bonding for diatomic molecules and ions which involve two different atoms. Such molecules and ions are called **heteronuclear systems**. Initially, we shall use hydrogen chloride as an example of such a system. The valence electron configuration of the hydrogen atom is $1s^1$, and the chlorine atom is $3s^23p^5$, so that each atom has one unpaired electron available for covalent bonding.

Bond Polarity

When two different types of atoms form an electron-pair bond, Lewis recognized that the two electrons would be shared unequally by the two atoms. The electron pair would be displaced more towards one atom than towards the other atom. For H_2 and HCl , Lewis wrote the valence formulas as:

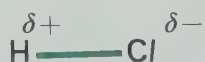


In the H_2 formula, the electron pair is symmetrically placed between the hydrogen atoms, but for HCl , the electron pair is displaced towards the chlorine atom. This displacement of the electron pair must produce a partial positive charge on the hydrogen atom, and a partial negative charge on the chlorine atom. To indicate this charge displacement, we may use either the formula above, or any of the following procedures:

- Put an arrowhead on the bond pointing in the direction of the charge displacement, i.e. in the case of HCl , towards the chlorine atom.



- Indicate partial positive and negative charges on the two atoms, by means of the symbols:



- Write down two valence structures, one of which involves equal sharing of the electron pair, and the other indicating complete displacement or transfer of the electron pair onto one of the atoms, thereby forming an anion and a cation. These structures, called **covalent** and **ionic** structures, are the following:



We then assume that the electron distribution of the bond is intermediate between that of either structure, neither structure alone represents the actual distribution of electrons in the bond. To obtain this, we must 'mix' the two valence structures. This 'mixing' of valence structures is called **resonance**.

This 'mixing' or resonance does not mean that for some of the time the molecule is covalent, and for the rest of the time it is ionic; nor does it mean that the electron distribution of the molecule is oscillating between that of the covalent structure, and that of the ionic structure. It does mean that the molecule has bond properties which are intermediate between those which are implied by each structure, and that neither alone is adequate.

There is neither a complete transfer of the pair of electrons to the chlorine atom, nor equal sharing of the pair of electrons by the hydrogen and chlorine atoms. The pair of electrons in this bond is more nearly associated with the chlorine atom. This type of bond is described as a covalent bond, with some ionic character.

The unequal sharing of the electron pair in the bond of HCl, and the consequent creation of partial positive and negative charges on the hydrogen and chlorine atoms, has an effect which may be detected experimentally. If the HCl molecule is placed in an electric field, it tends to align itself in such a way as to lower its energy.

Such a molecule is said to be **polar**. The measure of the tendency of a polar molecule to line up in an electric field, gives a quantity called the **electric dipole moment**.

Dipole Moments

For diatomic molecules, polar bonds constitute what are called *electric dipoles*. An electric dipole consists of equal positive and negative charges ($+ne$ and $-ne$) separated by a distance R .

For a diatomic molecule, this distance is the bond length.

The product of ne with R defines the magnitude of the dipole moment μ , in which e is the unit of charge (1.602×10^{-19} coulomb).

$$(+ ne) \text{---} \overset{R}{\mu = neR} \text{---} (- ne)$$

Figure 6.

In an electric field, an electric dipole will experience a torque, as shown in figure 7, and will orientate itself so that its energy is a minimum. One can measure the dipole moment from this orientation effect. In table 3, we report some measured dipole moments. If we assume here that the magnitude of the measured dipole moment depends only on n and R , then we find that alkali halides and hydrides are highly polar molecules, whereas hydrogen halides are rather less polar. Using the experimental dipole moments and the bond lengths, we have calculated the values of ne .

Table 3. Dipole moments for some polar molecules

	μ	R (μm)	$n = \frac{\mu}{Re}$
HF	1.91	92	0.43
HCl	1.07	127	0.18
HBr	0.79	142	0.12
HI	0.38	162	0.05
LiF	6.28	156	0.84
LiCl	7.09	202	0.73
NaF	8.12	193	0.88
NaCl	8.97	236	0.79

The unit of dipole moment is the Debye.

One Debye = 3.34×10^{-30} Cm.

Polyatomic molecules may or may not have dipole moments. Many very symmetrical molecules, e.g. CO_2 which is linear, have no dipole moments, even though their bonds may be polar. This is because the resultant moments (the vector sum of the moments for each of the bonds) are zero.

For many polyatomic molecules, e.g. NH_3 and H_2O , some of the dipole moment may not arise from the polar character of the bonds. Some or all of their lone-pair electrons may have considerable 'polarity', but we will not discuss this matter here.

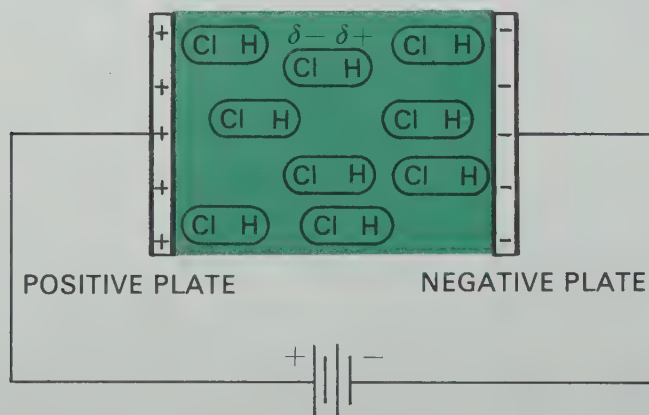


Figure 7. Alignment of electric poles (polar HCl molecules) in an electric field

Electronegativity

How can we determine the direction of the displacement of the bonding electrons? One method is to introduce the concept of **electronegativity**.

Electronegativity means an estimate of the relative ability of an atom to attract electrons to itself when forming a bond with another atom.

The electronegativity of atom A is written X_A ; the electronegativity of atom B is written X_B . When X_A is greater than X_B ($X_A > X_B$), the atom A has a greater ability to attract an electron than atom B.

For the HCl molecule we might expect the electronegativity of chlorine, X_{Cl} , to be greater than the electronegativity of hydrogen, X_H , i.e. $X_{Cl} > X_H$.

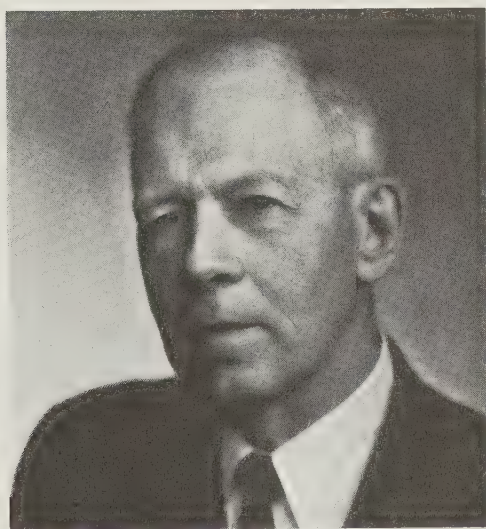


Figure 8. Robert S. Mulliken, who was born in 1896, was awarded a Nobel Prize in chemistry for his contributions to the understanding of chemical bonding and the behaviour of electrons in molecules. From Newberryport, Massachusetts, Mulliken graduated from the Massachusetts Institute of Technology, where his father was professor of organic chemistry. He describes his work as 'trying to understand what electrons in molecules are doing.'

The American scientist, Robert S. Mulliken (b.1896), proposed that electronegativity be defined as proportional to the sum of the ionization energy and the electron affinity of an atom. The ionization energy gives a measure of the ability of the atom to hold an electron. The electron affinity gives a measure of the ability of the atom to attract an extra electron to itself. An atom such as chlorine with a very high ionization energy and a high electron affinity will have a large electronegativity.

During the early 1930s, Linus Pauling (b. 1901), estimated the electronegativity of an atom by comparing the bond energies of certain molecules containing that atom (see Table 4). On this scale, fluorine, the most electronegative atom, has a value $X_F = 3.98$.

Table 4. Electronegativity values for some elements

H						
2.20						
Li	Be	B	C	N	O	F
0.98	1.57	2.04	2.55	3.04	3.44	3.98
Na	Mg	Al	Si	P	S	Cl
0.93	1.31	1.61	1.90	2.19	2.58	3.16
K	Ca	Ga	Ge	As	Se	Br
0.82	1.00	1.81	2.01	2.18	2.55	2.96
Rb	Sr	In	Sn	Sb	Te	I
0.82	0.95	1.78	1.96	2.05	2.10	2.66
Cs	Ba	Tl	Pb	Bi	Po	At
0.79	0.89	2.04	2.33	2.02	2.0	2.2

The alkali atoms, lithium, sodium, potassium, and so on, which have very small ionization energies, and small electron affinities, have the least ability to attract electrons in bonds. As a result, they have small electronegativities, for example, $X_K = 0.82$.

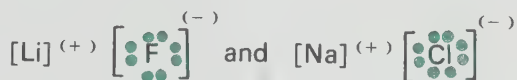
In the case of sodium, $X_{Na} = 0.93$, and chlorine, $X_{Cl} = 3.16$, the difference in the electronegativities is so large that there is virtually a complete transfer of the electron-pair bond. There are intermediate cases in which the bond between dissimilar atoms, such as MgS, is better described as covalent with some ionic character. Bonds between atoms which have the same electronegativity value are pure covalent bonds, e.g. Cl — Cl.

Exercises

- 9** Use the electronegativity table to discuss qualitatively the expected polarity of the bonds of NaF, NaH, HF, H₂O, H₂S, NH₃, PH₃, PF₃, CH₄ and NO. (The structures of the triatomic and polyatomic molecules are given on page 26. But you may be able to write them down without reference.)
- 10** For each of NaF, NaH and HF, indicate four different ways of showing the bond polarity.

Ionic Bonding

If we examine the dipole moments of LiF and NaCl in table 3, we find that they are large in magnitude. The electronegativities of the alkali metals in table 4 are much smaller than those of the halogens. These considerations suggest that the bonds of LiF and NaCl are highly polar, and therefore ionic valence structures such as:



may be reasonable representations of the electronic structures.

In these valence structures, there is no electron sharing, and the bonding arises from the electrostatic attraction between the oppositely charged ions.

This type of bonding is called ionic or **electrovalent bonding**, and we shall now discuss it in relation to the theories of Lewis and Kossel.

Lewis and Kossel recognized that the noble gases have stable arrangements of electrons. They suggested that atoms of many elements could achieve the stability of noble gases by either gaining or losing electrons.

Sodium with an atomic number of 11 has 11 electrons in the orbitals surrounding the nucleus. The sodium ion, Na^+ , has 10 electrons and is isoelectronic with the noble gas neon, which has an atomic number of 10. Chlorine with an atomic number of 17 has 17 electrons in the orbitals surrounding the nucleus. The chloride ion Cl^- , has 18 electrons and is isoelectronic with the noble gas argon which has an atomic number of 18.

If ionization energies are small, it is easy to form positive ions, or cations, from free atoms. Table 1 shows that the alkali metals Li and Na have small 2s or 3s ionization energies. Therefore, the

cations Li^+ and Na^+ may be involved in ionic bonding.

For Mg, the ionization energies for $\text{Mg} \rightarrow \text{Mg}^+$ and $\text{Mg}^+ \rightarrow \text{Mg}^{2+}$ are both small (735 and 1450 kJ mol^{-1}). Therefore, it is easy to form the cation Mg^{2+} which is isoelectronic with an atom of the noble gas Ne. Other metals also have one or more ionization energies which are small, and atoms of non-transition metals can easily form cations which are isoelectronic with one of the noble gas atoms. But whenever the metal ion has a noble gas configuration (e.g. $1s^2$ for Li^+ and $1s^2 2s^2 2p^6$ for Mg^{2+}), the energy which is needed to ionize another electron is very large. Thus for $\text{Li}^+ \rightarrow \text{Li}^{2+}$, the ionization energy is 7293 kJ mol^{-1} . Because of this, ions such as Li^{2+} and Mg^{3+} do not participate in ionic bonding under normal conditions.

The ease of formation of an anion is determined by the **electron affinity** of a gaseous atom. Halogens have large electron affinities compared with those of other elements, and therefore a halogen atom can acquire a noble gas configuration easily by gaining an electron to form a halide anion, such as Cl^- . Table 5 lists the noble gases and some well-known ions which are isoelectronic with them. Ionic bonding is possible between many of the anions and cations listed in the table. For example, the bonding of lithium fluoride LiF , may be described by the electrostatic attraction between the lithium ion Li^+ , and the fluoride ion F^- .

Table 5. Noble gases and some isoelectronic ions

Noble gas	Atomic number	Isoelectronic ions
Helium	2	H^- , Li^+ , Be^{2+}
Neon	10	O^{2-} , F^- , Na^+ , Mg^{2+} , Al^{3+} , NH_4^+ , H_3O^+ , OH^-
Argon	18	S^{2-} , Cl^- , K^+ , Ca^{2+}
Krypton	36	Br^- , Rb^+ , Sr^{2+}
Xenon	54	I^- , Cs^+ , Ba^{2+}
Radon	86	Ra^{2+}

Many polyatomic anions, such as the permanganate ion MnO_4^- , the dichromate ion $\text{Cr}_2\text{O}_7^{2-}$, the carbonate ion CO_3^{2-} , and the sulphate ion SO_4^{2-} , may be involved in ionic bonding with suitable cations. But within these anions, e.g. SO_4^{2-} , the bonding is not ionic even though their bonds are polar.

In all cases of ionic bonding, extra stability is achieved when crystal lattices with millions of ions are formed.

It should be obvious that ionic molecules can behave as electrolytes in aqueous solutions. However, not all molecules with polar bonds are electrolytes. For example, both HCl and CH₃Cl have polar bonds, but only HCl forms ions in aqueous solution. Why do these molecules differ in their properties?

Exercises

- 11 What factors lead to the formation of polar and ionic bonds? Compare and contrast the expected properties, such as dipole moment and solubility in water, of H₂, F₂, Na₂, HF, NaF, NaH, CH₃F and NH₄F.
- 12 Would the anions O³⁻, F²⁻, H²⁻, He⁻ and Ne⁻ be involved in ionic bonding?
- 13 Which of Ca⁺Cl⁻ and Ca²⁺(Cl⁻)₂ is the more stable? What information is needed to answer this question?

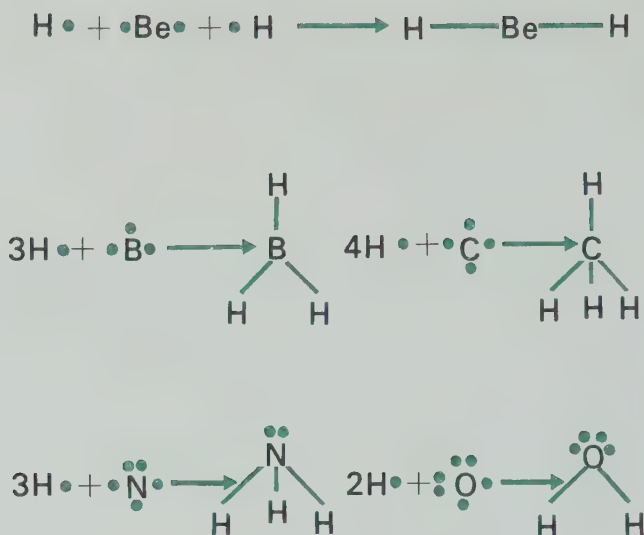
Polyatomic Molecules with Single Bonds and One-Electron Bonds

We shall now discuss the extension of the Lewis theory of electron-pair bonds to triatomic and polyatomic molecules.

Usually, an electron pair will be shared unequally between two different types of atoms of any molecule, i.e. the bond will be polar, but we shall not emphasize this aspect of bonding. In the valence formulas, valence lines are used to represent electron-pair bonds.

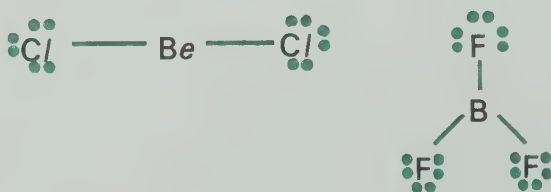
Some Triatomic and Polyatomic Hydrides and Halides

The molecules, beryllium hydride BeH₂, boron hydride BH₃, methane CH₄, ammonia NH₃, and water H₂O, have hydrogen atoms bonded to a second-row atom. Table 2 lists the electron configurations for the second-row atoms. We may form covalent bonds by assuming that these atoms can share some or all of their valence electrons with those of the hydrogen atoms.



The nitrogen atom of NH_3 uses three of its five valence electrons to form bonds to the hydrogen atoms. The remaining two electrons are non-bonding or lone-pair electrons. For H_2O , the oxygen atom has four non-bonding electrons, i.e. two lone-pairs of electrons.

BeH_2 and BH_3 have not yet been prepared as stable molecules, but beryllium chloride BeCl_2 , and boron trifluoride BF_3 have been made. In their Lewis formulas, each halogen atom has three lone-pairs of electrons.



As an exercise, you may derive Lewis formulas for CCl_4 , NF_3 , F_2O , PF_3 , PH_3 and H_2S .

The Octet Rule

If you examine the valence formulas which are shown in the previous section, you will find that the carbon, nitrogen, oxygen and fluorine atoms have acquired the electron configurations of the noble gas neon; they have eight electrons arranged around their atomic symbol or kernel. As we have found previously,

Lewis suggested that the neon configuration represents a particularly stable group of electrons. Therefore, whenever we construct Lewis valence formulas for molecules with carbon, nitrogen, oxygen or fluorine atoms, we should endeavour to have an **‘octet’ of electrons** arranged around the kernel (i.e. the nucleus plus inner shell electrons), for these atoms.

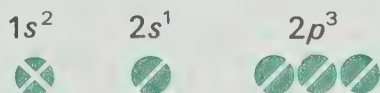
This rule was called the *‘rule of eight’* by Lewis, and the ‘octet rule’ by Langmuir in 1919. The octet rule does not apply to the beryllium and boron atoms in the Lewis formulas that we have given for BeH_2 , BeCl_2 , BH_3 and BF_3 .

Carbon Valence of Four

Valence formulas which involve carbon atoms show that the carbon valence is four. In the Lewis theory, the carbon atom must use four unpaired electrons to form covalent bonds with the unpaired electrons of other atoms. However, if we examine the electronic configuration for the ground state of the carbon atom, namely $1s^2 2s^2 2p^2$ (see figure 1), we find that there are only two unpaired electrons which occupy two of the three $2p$ atomic orbitals.



In order that the carbon atom may have four unpaired electrons, we must assume that one of the $2s$ electrons is ‘excited’ or ‘promoted’ into the vacant $2p$ atomic orbital. This promotion leaves each of the $2s$ and three $2p$ atomic orbitals singly occupied.



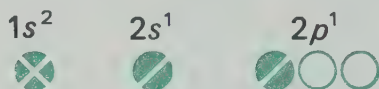
To indicate this promotion, we may write:



The valence of two for the beryllium atom in BeF_2 and BeH_2 may be similarly explained. Beryllium has a ground state electronic configuration of $1s^2 2s^2$ with no unpaired electrons.



On promotion of a $2s$ electron to a vacant $2p$ atomic orbital, the configuration becomes $1s^2 2s^1 2p^1$ with two unpaired electrons.



The valence of three for the boron atom in BH_3 may be explained by considering the ground state electronic configuration of boron, namely, $1s^2 2s^2 2p^1$ with one unpaired electron.

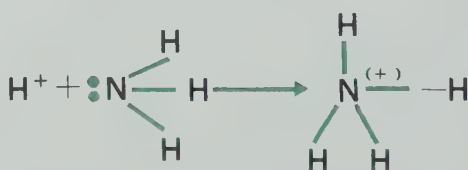


The promotion of a $2s$ electron to a vacant $2p$ atomic orbital makes the configuration $1s^2 2s^1 2p^2$ with three unpaired electrons.

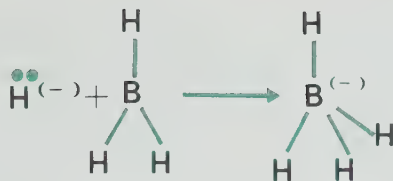


Isoelectronic Molecules

Each of the molecules CH_4 , NH_3 , H_2O and HF , has eight valence electrons, and therefore these molecules are isoelectronic with each other and also with the neon atom. The anion BH_4^- and the cations NH_4^+ and H_3O^+ , are also isoelectronic with these systems. We may obtain the two cations by adding a proton (H^+) to NH_3 and H_2O .



A lone-pair of electrons on the nitrogen atom of NH_3 and the oxygen atom of H_2O is used to form the bond with the vacant $1s$ orbital of the hydrogen ion. To obtain a valence formula for the anion BH_4^- , the two electrons of the hydrogen anion H^- , are used to form the covalent bond with the vacant $2p$ orbital of BH_3 .



Why are the positive or negative charges placed on the nitrogen, oxygen and boron atoms?

Exercises

- 14 Write down Lewis valence formulas for BF_4^- , CF_4 , NF_3 and OF_2 . Which of these systems are isoelectronic? How many lone-pairs of electrons does each system have?
- 15 Are the molecules C_2H_6 , N_2H_4 , H_2O_2 and F_2 isoelectronic? Write the Lewis valence formulas, assuming that the carbon, nitrogen and oxygen atoms are bonded to three, two and one hydrogen atoms respectively.

Shapes of Molecules

Table 6 gives measured bond lengths and bond angles for a number of molecules and ions. Thus, we find that beryllium chloride, BeCl_2 , is a linear molecule, whereas H_2O and F_2O are bent. Each of CH_4 , NH_4^+ , BH_4^- , CF_4 and BF_4^- has bond angles of $109^\circ 28'$, which are those of a regular tetrahedron. The bond angles of NH_3 are a little smaller than those of NH_4^+ , but indicate that the molecule is pyramidal. On the other hand, BF_3 is found to be planar with all bond angles equal to 120° .

Why do the shapes of these molecules and ions vary? We shall now describe a simple theory which can account qualitatively for the observations.

In 1940, the English chemists N. V. Sidgwick and H. M. Powell, indicated that the position of bonds about an atom is determined by the number of electron pairs associated with that atom in the molecule. The theory was developed more fully in 1957 by the Canadian chemist R. J. Gillespie, and the Australian chemist R. S. Nyholm. We shall describe relevant aspects of the theory.

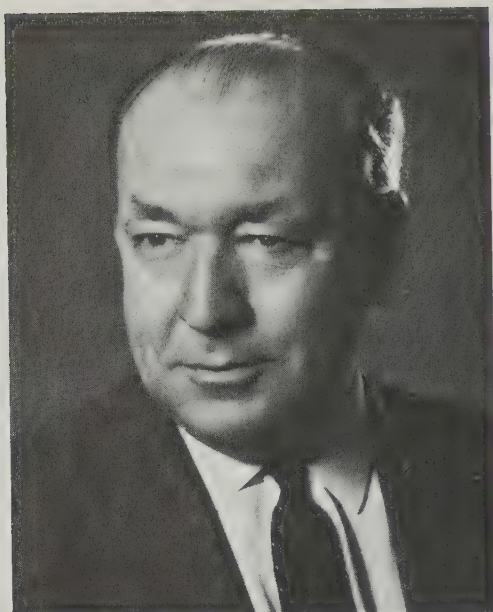


Figure 9. Sir Ronald Nyholm was born in Broken Hill in 1917, and attended school there. He won a scholarship to the Sydney University, and studied inorganic and physical chemistry. Nyholm gained a Ph.D. degree and a D.Sc. degree from the University College in London. Nyholm's main fields of research are inorganic chemistry, especially the study of complex compounds of transition metals and the chemistry of compounds containing metal-metal bonds. Nyholm was elected a Fellow of the Royal Society in 1958, and was created a Knight Bachelor in 1967. He died as a result of a car accident in December 1971.

In the Lewis valence formulas, pairs of valence electrons are arranged around the atomic kernel (i.e. the nucleus plus inner shell electrons) of each atom. According to Gillespie and Nyholm, the most stable arrangement of these electron pairs should occur when the electrostatic repulsions between them are a minimum. For two, three and four pairs of electrons, these repulsions are minimized when the electron pairs occupy positions on opposite sides of the atomic kernel (designated as A in the diagrams below); at the corners of an equilateral triangle; and at the corners of a tetrahedron.



This theory predicts that BeH_2 and BeCl_2 , each with two pairs of bonding electrons in the Lewis formulas, should be linear molecules. BH_3 and BF_3 have three pairs of bonding electrons and so they should be planar molecules with bond angles of 120° . CH_4 , NH_4^+ , BH_4^- , CF_4 and BF_4^- have four pairs of bonding electrons distributed around the kernel of the non-hydrogen atom, and therefore these molecules and ions are predicted to be tetrahedral in shape. In table 6, the reported shapes are in agreement with these predictions.

Table 6. Molecular geometries

	Bond Angles	Bond Lengths (pm)	Shape
BeH_2	—	—	
BeCl_2	180°	—	linear
BH_3	—	—	
BF_3	120°	$\text{BF} = 130$	planar
CH_4 , $(\text{NH}_4^+, \text{BH}_4^-)$	$109^\circ 28'$	$\text{CH} = 109$	regular tetrahedron
CF_4 (BF_4^-)	$109^\circ 28'$	$\text{CF} = 131$	regular tetrahedron
NH_3	107.3°	$\text{NH} = 101$	trigonal pyramid
NF_3	102.1°	$\text{NF} = 137$	trigonal pyramid
H_2O	104.5°	$\text{OH} = 96$	bent, V-shape
F_2O	103.2°	$\text{OF} = 142$	bent, V-shape

NH_3 , NF_3 , H_2O and F_2O also have four pairs of valence electrons distributed around the nitrogen and oxygen kernels of their Lewis formulas. One or two of these pairs is a lone-pair of electrons and the others are bonding pairs. The bond angles of these molecules are all smaller than the $109^\circ 28'$ for the regular tetrahedron. These observations may be accounted for by the following improvement to the Gillespie-Nyholm theory. We quote directly from their paper which was published in *Quarterly Reviews*, 11, 344 (1957).

This simple theory can be considerably improved qualitatively by assuming that electrostatic repulsions between the electron pairs in a valency shell decrease in the order: (lone-pair—lone-pair) > (lone-pair—bond-pair) > (bond-pair—bond-pair). This can be understood by picturing the lone-pairs as closer to the nucleus than the bonding pairs, which may be imagined pulled out to some extent by the other nucleus with which they are forming a bond. Thus the lone pairs will be closer to each other than the bonding pairs, and so will repel each other more strongly.

On passing from methane to ammonia, we replace a bonding pair by a lone pair, which repels the remaining three bond pairs somewhat more than the original bond pair, so causing the bond angle to decrease from the tetrahedral value of $109^\circ 28'$. On passing from ammonia to water we replace another bond pair by a lone pair and the bond angle decreases further.

Exercises

- 16 Compare and contrast the bonding and expected shapes of AlCl_3 , SiCl_4 , PCl_3 and SCl_2 .
- 17 In table 6 the reported bond angles of NF_3 and F_2O are smaller than are those of NH_3 and H_2O . Can you suggest a possible reason for this?

Electron-Pair Bond Formulas for Pentafluorides and Hexafluorides

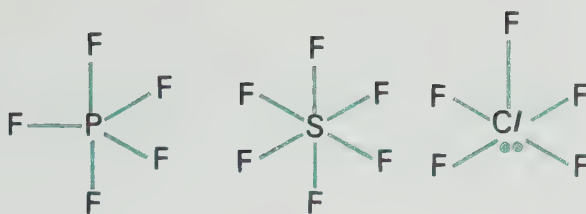
In contrast to the atoms of second-row elements, third and higher-row atoms can often form stable molecules in which these atoms are bonded to five or more other atoms. For example, the molecules PF_5 , SF_6 , ClF_5 , IF_7 and XeF_6 are known. The valence electron configurations for the phosphorus, sulphur and chlorine atoms are shown below.

phosphorus $3s^23p^3$

sulphur $3s^23p^4$

chlorine $3s^23p^5$

Therefore, they have 5, 6 and 7 valence electrons. We may assume that these atoms use 5, 6 and 5 of their valence electrons to form electron pair bonds with the same number of fluorine atoms.



For convenience, we have not indicated the lone-pairs of electrons on the fluorine atoms in the formulas for the molecules. We have however, retained the lone-pair of electrons on the chlorine atom of ClF_5 . This is because the presence of this lone-pair considerably affects the shape of the molecule.

Exercise

18 Write the valence formulas for IF_7 and XeF_6 , indicating the number of lone-pair electrons on the iodine and xenon atoms.

By using only the $2s$ and $2p$ atomic orbitals, we have found that second-row atoms cannot form more than four electron-pair bonds. This is also true for third-row atoms if the $3s$ and $3p$ atomic orbitals are used. How then does phosphorus acquire a valence of five? One answer to this question is obtained by noting that phosphorus has $3d$ as well as $3s$ and $3p$ atomic orbitals in its valence shell.



If we assume that a $3s$ electron is promoted into one of the $3d$ atomic orbitals the promoted phosphorus atom will have five unpaired electrons, and can then form five electron-pair bonds.



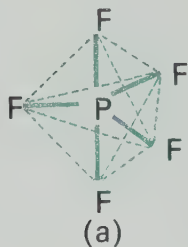
We write the promotion as shown:



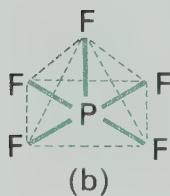
Similar promotions of electrons into higher energy orbitals can account for valencies greater than four for the sulphur atom in SF_6 ; the chlorine atom in ClF_5 ; the iodine atom in IF_7 ; and the xenon atom in XeF_6 .

The Shape of PF_5

Using these valence formulas for PF_5 we can predict the shapes of the molecule. There are three structures which we might examine.



(a) This structure has the shape of two pyramids, each with an equilateral triangle as a base, placed base to base. This structure is called a trigonal bipyramid. Three bond angles are 120° ; the other two bond angles are 90° .



(b) This structure has the shape of a pyramid with a square base and is called a square pyramid. All bond angles are 90° .

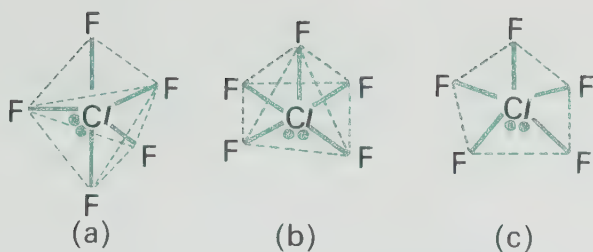


(c) This structure has all the bonds in one plane, and since there are five bonds, the bond angle is 72° .

Which shape has the lowest energy? Using the Gillespie-Nyholm theory, the repulsions between pairs of electrons need to be a minimum. This occurs for structure (a), because the bonds are on the average further apart than they are for structure (b) and for structure (c). Appendix I considers an alternative theory on the structure of PF_5 .

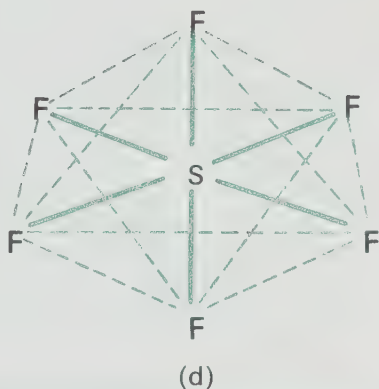
The Shapes of ClF_5 and SF_6

We may consider three shapes for ClF_5 . They are similar to the structures given for PF_5 , except for the presence of the lone-pair of electrons on the chlorine atom. Minimum repulsions between the six pairs of electrons occur for the second structure, rather than for the first structure.



For ClF_5 the angles that the four planar bonds make with the axial bond are a little less than 90° . This could be because the lone-pair of electrons on the chlorine atom repels the planar bonds more strongly than does the electron pair of the axial bond. A similar effect has been noted already for ammonia NH_3 , which has smaller bond angles than does the ammonium ion NH_4^+ .

For SF_6 , minimum repulsions between the six SF bonds occur when the molecule has the shape of the octahedron of (d). This structure has the shape of two pyramids, each with a square base, and has 90° bond angles.



Exercise

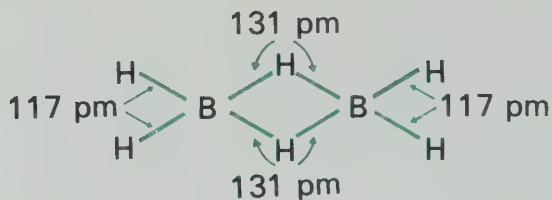
19 For the following pairs of molecules or ions, write down valence formulas and contrast their predicted shapes:

- (i) PCl_5 and IF_5
- (ii) SF_4 and XeF_4 ,
- (iii) AlCl_3 and PCl_3 .

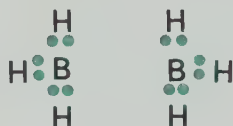
Electron Deficient Molecules

For a number of molecules, there are not enough electrons to form two-electron bonds between all pairs of adjacent atoms, no matter what orbitals we use. Such molecules are called **electron deficient molecules**. The simplest example is H_2^+ , with one electron.

Perhaps diborane B_2H_6 , is the most well known polyatomic molecule which is electron deficient. Each boron atom is bonded to four hydrogen atoms. The bond lengths are:

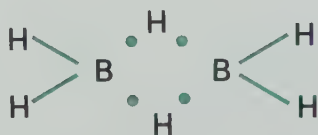


Diborane B_2H_6 , has twelve valence electrons and Lewis proposed the following valence formula:



Lewis noted that this formula does not indicate bonding between the two BH_3 halves of the diborane molecule.

Perhaps the simplest structure for B_2H_6 is:



This was suggested by Linnett in 1964. The structure is compatible with the observed bond lengths if we assume that two-electron-bonds are shorter than one-electron-bonds.

Exercise

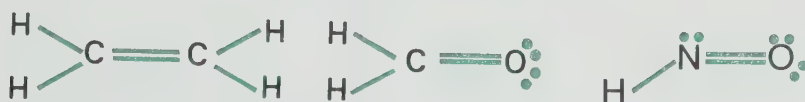
- 20** Compare the bonding of C_2H_6 and B_2H_6 . Name some other molecules which are isoelectronic with B_2H_6 .

Polyatomic Molecules with Double Bonds and Triple Bonds

In the previous section we studied the bonding for molecules which have single bonds. We shall now examine some molecules whose Lewis formulas possess double bonds and triple bonds.

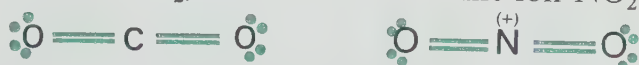
Ethylene (ethene)

The carbon atom with a valence of four, may form four electron-pair bonds in various ways. For methane CH_4 , carbon tetrafluoride CF_4 , and ethane C_2H_6 , carbon may form four single bonds. Alternatively, carbon may form two single bonds and a double bond. For the Lewis formula of O_2 , a double bond can consist of two electron-pair bonds. Such a bond occurs in the Lewis formulas for ethylene (C_2H_4) and formaldehyde (HCOH). These three molecules have twelve valence electrons and are isoelectronic with nitroxyl (HNO). The Lewis valence formulas for the molecules of ethene, formaldehyde and nitroxyl are:



Carbon Dioxide

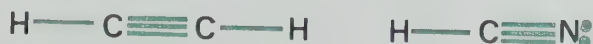
Instead of forming a double bond and two single bonds, the carbon atom may form two double bonds, as occurs in the Lewis formulas for carbon dioxide CO_2 , and the isoelectronic ion NO_2^+ .



To minimize repulsions between pairs of bonding electrons, the molecule and ion are linear.

Molecules with Triple Bonds

Acetylene (ethyne) C_2H_2 , has ten valence electrons and it is isoelectronic with the nitrogen molecule N_2 . We have found that N_2 has a triple bond which consists of three electron pairs. The Lewis formula for C_2H_2 has a similar bond between the two carbon atoms. Both molecules are isoelectronic with hydrogen cyanide HCN , and we show the Lewis formulas for all three systems. Can you predict the shapes of HCN and C_2H_2 ?



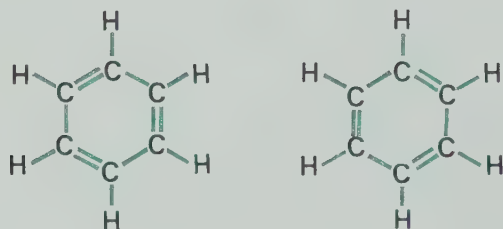
Resonance

Benzene

When we discussed the HCl molecule on page 18, we used the term *resonance*. Resonance meant that two Lewis valence formulas were needed to account for the electron distribution in the molecule. One formula alone was not satisfactory. We shall develop the resonance concept further by examining the Lewis formulas and bond properties of benzene (C_6H_6).

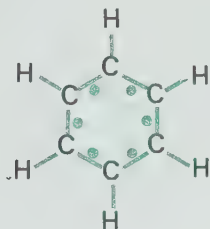
Chemical and physical evidence suggests that the six carbon atoms of benzene are bonded to form a regular hexagon, and that each carbon atom is bonded to one hydrogen atom. With a valence of four, each carbon atom must form one single bond and one double bond with the two carbon atoms that are adjacent to it.

Two valence structures with the bonds arranged in different ways can be derived. These structures are called Kekulé structures, in honour of the German chemist who proposed them in 1865.

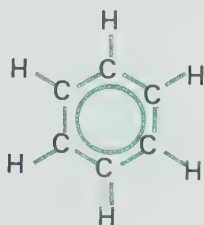


Using one of these structures to represent the molecule, we would expect the three carbon-carbon double bonds $C=C$, to have lengths which are similar to that of the carbon-carbon double bond of ethene, namely 134 pm. The three carbon-carbon single bonds $C-C$, would be longer—151 pm. However, all carbon-carbon bonds have lengths of approximately 140 pm. Therefore, one Kekulé structure alone is not able to show the equality in length of all six bonds. This equality is only evident if we take both structures together. We may therefore speak of ‘resonance’ between the two Kekulé structures, meaning (as we have already indicated) that both structures are needed in order to account for the electron distribution of the molecule.

Instead of using the two Kekule structures with electron-pair bonds, Linnett in 1960, suggested that we use a single valence structure which has both electron-pair bonds and one-electron bonds. This structure indicates immediately the equivalence in length of all the carbon-carbon bonds.



Many chemists also use the structure in which the circle represents the six electrons that are responsible for double bonding.



The NSCM Booklets C13 The Chemistry of Carbon—Part I, and C14 The Chemistry of Carbon—Part II discuss the benzene molecule more fully.

Resonance and the Nitrite Anion

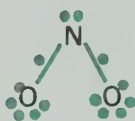
The nitrite anion (NO_2^-) is another system for which resonance between two Lewis structures is needed in order to describe the electronic structure of the ion. Starting with the nitrogen atom, N, the oxygen atom O, and the oxygen ion, O^- the valence formulas are:



Two Lewis valence formulas for NO_2^- can be constructed:



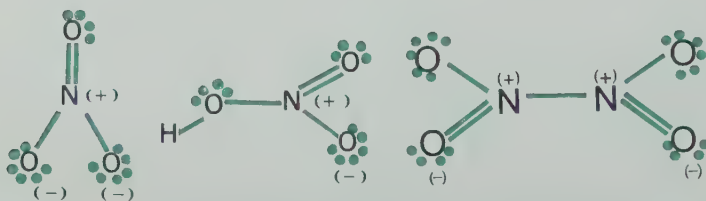
If either of these two formulas is used to represent the ion, we would expect the two nitrogen-oxygen bonds to have different lengths. However, the measured lengths are 124 pm for both bonds. Therefore, we need resonance between both structures in order to explain the equivalence in bond lengths. If we abandon the electron-pair Lewis structures and use the Linnett structure below, we can account for the bond properties.



Some Molecules and Ions with Tetravalent Nitrogen Atoms

If we re-examine the Lewis valence formulas for N_2 , NH_3 , NF_3 , HNO and NO_2^- we find that the nitrogen atom valence is three. For NH_4^+ and NO_2^+ , the nitrogen valence is four and in the Lewis formulas, the entity N^+ is bonded either to four hydrogen atoms with valencies of one, or to two oxygen atoms with valencies of two. We may recall that N^+ is isoelectronic with the carbon atom, and therefore we can understand why N^+ can form four electron-pair bonds. Numerous other systems exist in which the positive nitrogen ion (as N^+) is tetravalent in Lewis formulas. Some well-known examples are the nitrate anion (NO_3^-), nitric acid (HNO_3) and dinitrogen tetroxide (N_2O_4), whose valence formulas are shown:

Other equivalent valence formulas may be constructed.



Exercise

- 21 Since N^+ and C are isoelectronic, what ions and molecules containing carbon atoms are isoelectronic with NO_3^- , HNO_3 and N_2O_4 ? Write Lewis valence formulas for them.

Water, Hydrogen Bonding and Aquo-Ions

About 70% of the surface of the earth is covered by water, and about 60% by weight of our bodies is water. It is of interest then to consider the structure of water molecules in more detail.

A valence formula for H_2O is shown in figure 10. Each electron-pair bond arises from the sharing of an unpaired oxygen electron with a hydrogen electron. In table 4, the electronegativities of oxygen and hydrogen are 3.44 and 2.20 respectively, which indicate that oxygen is considerably more electronegative than hydrogen. Therefore, we would expect the $\text{O} - \text{H}$ bonds of H_2O to be polar, and bonding electron pairs to be displaced towards the oxygen atoms. This displacement would produce a fractional negative charge on the oxygen atom, and fractional positive charges on the hydrogen atoms. These charges are indicated in figure 10.

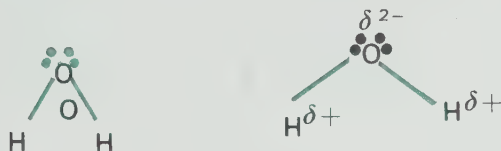


Figure 10.

Hydrogen Bonding

When water freezes, ice is formed. Ice consists of millions of H_2O molecules that are weakly bonded to form a tetrahedral array, as shown in figure 11. The broken lines in the figure represent the weak bonds, the nature of which we shall discuss.

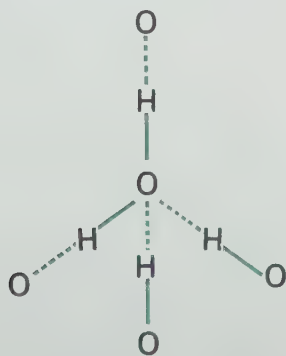


Figure 11.

Similarly, the formation of liquid water by condensation of steam also involves considerable aggregation of H_2O molecules.

The bonds between the H_2O molecules in water or ice are long (176 pm), compared to 96 pm for the O—H lengths of a single H_2O molecule. These long weak bonds are easily broken by melting the ice and boiling the water.

Other molecules such as NH_3 , H_2S , PH_3 and HF can also associate weakly to form molecular aggregates. In each case, the associated molecules involve hydrogen atoms and an electronegative atom. This type of association is called ‘hydrogen bonding’.

What is the Origin of Hydrogen Bonding?

For H_2O , we have shown that the oxygen and hydrogen atoms carry partial positive charges and negative charges. It is often assumed that the electrostatic attraction between the negatively charged oxygen atom of one H_2O molecule and a positively charged hydrogen atom of an adjacent H_2O molecule is mainly responsible for the hydrogen bonding. This attraction is shown in figure 12, and is called **dipole-dipole interaction**.

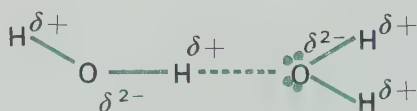
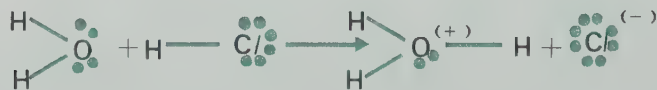


Figure 12.

The Proton in Water

In a solvent such as water, many polar molecules can ionize by reacting with H_2O molecules, thereby forming solvated anions and cations. We shall now discuss the solvated proton.

The reaction between HCl and H_2O may be represented as:



This is the process by which the **unsolvated** proton H_3O^+ (or the oxonium ion) is formed as previously studied. The oxonium ion may also be **solvated**, and the ions $\text{H}(\text{H}_2\text{O})_2^+$ and $\text{H}(\text{H}_2\text{O})_4^+$ are known. For $\text{H}(\text{H}_2\text{O})_2^+$, we may write down two equivalent valence

structures (see figure 13). Each of these consists of $\text{H}_3\text{O}^+ + \text{H}_2\text{O}$. The two OH bond lengths of the OHO group are equal, namely 123 pm, and we require resonance between structure (a) and structure (b) to account for the observation.

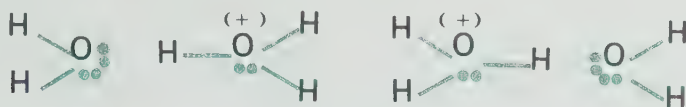


Figure 13.

Instead of resonance between the two Lewis formulas as shown in figure 13, we may use the Linnett formula illustrated in figure 14. We may also obtain this formula from the two H_2O molecules and proton, by delocalizing oxygen lone-pair electrons into the bond regions between the two oxygen atoms and the proton. The proton is bonded to the H_2O molecules by means of one-electron bonds.

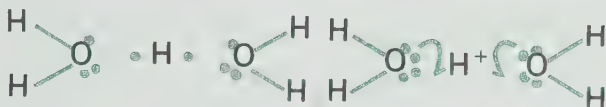


Figure 14.

Other Solvated Cations

Metal cations as well as protons, may also be solvated in aqueous solutions to form aquo cations. Anions may also be solvated. Some examples of solvated cations are $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and $\text{Ni}(\text{H}_2\text{O})_6^{2+}$.

There are two theories of cation- H_2O bonding. One of these is electrostatic. Cations can attract the oxygen atoms of the H_2O molecules, because the oxygen atoms carry partial negative charges. This attraction is shown in figure 15 for $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

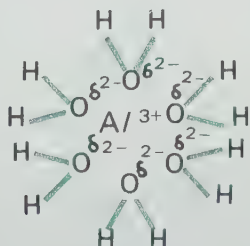


Figure 15.

Alternatively, Al^{3+} has vacant $3s$ and $3p$ atomic orbitals, and four oxygen atoms can use these orbitals to form four electron-pair bonds. (See figure 16.) These four electron-pair bonds can 'resonate' amongst the six AlOH_2 positions.

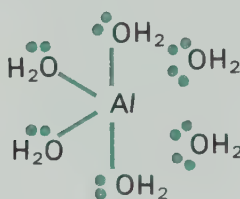


Figure 16.

This type of bond, which uses a lone-pair of electrons on one atom and a vacant atomic orbital on an adjacent ion or atom, is called a **co-ordinate** bond.

For $\text{H}(\text{H}_2\text{O})^+$, we have used valence structures which have either electron-pair bonds or one-electron bonds between the proton and the H_2O molecules. For metal aquo cations, we may also use similar types of structures. In figure 17 the H_2O molecules form one electron bond to the Al^{3+} .

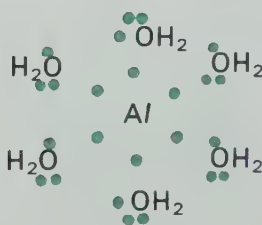


Figure 17.

Exercise

22 Discuss some bonding theories for $\text{Cu}(\text{NH}_3)_4^{2+}$ and $\text{Cl}(\text{H}_2\text{O})_4^-$.

Molecular Orbitals and Bonding for the Hydrogen Molecule

For the hydrogen molecule, we have given the Lewis theory of covalent bonding on page 7 . According to this theory, each hydrogen atom shares its electron with the other hydrogen atom to form an electron-pair bond. Now we shall consider how the electron sharing stabilizes the hydrogen molecule relative to two hydrogen atoms. To do so, it is necessary to learn more about electron orbitals. We should note that Lewis put forward his theory ten years before the concept of an orbital was developed.

1s Atomic Orbital and Charge Cloud for the Hydrogen Atom

In an atom or a molecule an electron ‘behaves’ as though it were a smeared-out charge cloud. For more details about this, read the NSCM Booklet C1 The Chemist’s View of the Atom. An orbital helps to define the charge cloud.

The charge cloud which is defined by the 1s atomic orbital of a hydrogen atom is shown in figure 18. We see that the charge cloud is dense near the atomic nucleus and as we go further out from the nucleus, the density of the electron charge cloud decreases. This density approaches zero as we go infinitely out from the nucleus (why?).



Figure 18. Electron charge clouds for (a) the hydrogen atom (b) the hydrogen molecule ion.

Molecular Orbital and Charge Cloud for the Hydrogen Molecule Ion

For the hydrogen atom, the electron ‘occupies’ the 1s atomic orbital. When the hydrogen molecule ion H_2^+ is formed, the electron orbital helps to define an electron charge cloud distribution around both protons of the ion. This orbital is called a **molecular orbital**, and its charge cloud is shown in figure 18.

Electron Charge Cloud for the Hydrogen Molecule

According to the atomic orbital theory, the number of electrons in any atomic orbital can be zero, one, or two. The same number of electrons can occupy a molecular orbital simultaneously. Therefore, the two electrons of H_2 can occupy the same molecular orbital, and we may assume that the charge cloud for each electron is the same as that of figure 18 for H_2^+ . The total charge cloud for the two electrons will then be twice as dense as that for the electron of H_2^+ . In figure 19 we show

- (a) the total charge cloud for the two electrons of H_2 , and, for comparison
- (b) the charge clouds for two hydrogen atoms, if we could imagine the two electrons still occupying atomic orbitals instead of the molecular orbital.

In both (a) and (b), the protons are assumed to be the same distance apart. (What distance should this be?)

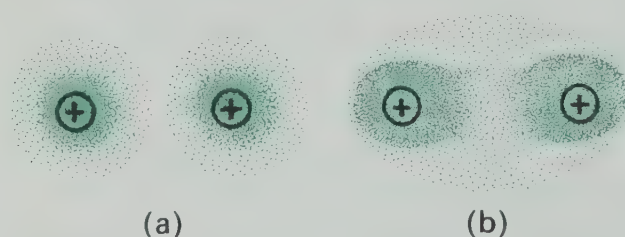


Figure 19. Electron charge clouds for (a) two hydrogen atoms (b) the hydrogen molecule.

When we compare (a) and (b) of figure 19, we find that *between* the protons of (a) the charge cloud is *denser* than it is at corresponding positions for (b). Therefore, on formation of the hydrogen molecule, we may say that some of the electron charge cloud has *accumulated* between the protons. Theoretical chemists have shown, by calculation, that this *accumulation of electron charge cloud between the protons* is chiefly responsible for covalent bonding, i.e. for binding two hydrogen atoms together.

Charge Accumulation and Covalent Bonding

How does this charge cloud accumulation between the protons produce the bonding, i.e. the stabilization or lowering of energy of the hydrogen molecule relative to two hydrogen atoms? Many chemists have given a reason such as the following:

In the hydrogen molecule, this charge cloud is attracted electrostatically by two protons. In separated hydrogen atoms, it would be attracted by one proton only. Therefore, this extra attraction that occurs for H_2 is responsible for bonding.

Such an appeal to electrostatics—but perhaps not always expressed in this manner—has been used very often. In 1962, the American theoretical chemist K. Ruedenberg, suggested that ‘certain ideas concerning the nature of the chemical bond need to be revised.’ He concluded (and showed for H_2) that electrostatics cannot account for the covalent bonding.

Figure 20. Professor Klaus Ruedenberg, who was born in Bielefeld, Germany in 1920, studied at the University of Chicago from 1948 till 1950. In Zürich, Switzerland, 1950, he gained a Ph.D degree in theoretical physics; he then became Associate Professor at Chicago, from 1951-55. From 1962 till 1964, Ruedenberg was Professor of Chemistry at the John Hopkins University. He has been Professor of Chemistry and Physics at Iowa State University of Science and Technology, at Ames, Iowa, since 1964. His special fields of study are molecular quantum mechanics, chemical bonding, molecular spectra, and quantum chemistry, and in particular, very detailed quantum mechanical mathematical studies of molecules.



In his 1962 paper (which is very long and mathematical) Ruedenberg calculated the kinetic energy and the electrostatic potential energy of the charge cloud which accumulates between the protons. The results of his calculations show that on formation of the hydrogen molecule, the *kinetic energy* of this charge cloud (not its potential energy) decreases, thereby stabilizing the molecule. Therefore, Ruedenberg considers that this lowering of kinetic energy is primarily responsible for covalent bonding.

To understand better this lowering of kinetic energy, we need to know more about quantum mechanics. Here, we can only say that an electron has both particle (mass) and wave (wavelength) properties. Because of this wave-particle duality, it can be deduced that if we increase the amount of available space in which the electron charge cloud moves, we lower its kinetic energy. (If you study physics you should be able to prove this result by appeal to the de Broglie relationship.) When we examine the charge clouds of figure 19, we find that the charge between the protons is denser and more 'spread out' in (a) for the molecule than in (b) for the atoms. Therefore, the **accumulated charge** of (a) has 'more room to move in' and therefore has its kinetic energy lowered. Ruedenberg stresses that covalent bonding is a quantum mechanical, rather than (as is usually supposed) an electrostatic phenomenon.

Analogy between Covalent Bonding and Space Travel

In a paper which was published in February 1971, Professor Klaus Ruedenberg and M. J. Feinberg suggested that this kinetic energy decrease has an analogy with space travel. Their discussion goes as follows:

Consider a spacecraft circling Earth in a stable orbit, for example, one hundred miles above Earth. Suppose the pilot of the spacecraft wants to go into a stable orbit with less total energy, for example, fifty miles above Earth. To do this, he must fire a retrorocket which momentarily slows down the craft, that is, **reduces its kinetic energy**. The spacecraft goes into the lower energy orbit because of the pull of gravity. Therefore, the **total energy** of the spacecraft is reduced, because of the reduction in kinetic energy after the firing of the retrorocket. The high and low energy orbits correspond to the energies of the two hydrogen atoms and the hydrogen molecule respectively. *A Paradox:*

The **total energy** of the spacecraft is greater one hundred miles above Earth than it is fifty miles above Earth. The spacecraft has a higher kinetic energy and a lower potential energy in the fifty mile orbit. But the retrorocket reduces the kinetic energy in the higher energy orbit.

Explain this 'paradox'.

Although we have not indicated it, Ruedenberg and Feinberg describe a similar type of paradox which occurs in the formation of a molecule.

Molecular Orbitals and Charge Clouds for Polyatomic Molecules

The electron configuration of an atom may be expressed in terms of the atomic orbitals that are occupied. We may also construct electron configurations for molecules in terms of molecular orbitals for the electrons. We cannot go into this here, except to say that for each molecular orbital, the associated charge cloud for the electron may be distributed over two or more atomic centres. If the charge cloud is distributed over only two atomic centres, it is said to be a **localized** charge cloud. If it is distributed over more than two atomic centres, it is called a **delocalized** charge cloud. In figure 21 we show some localized charge clouds for CH_4 , H_2O and C_2H_4 .

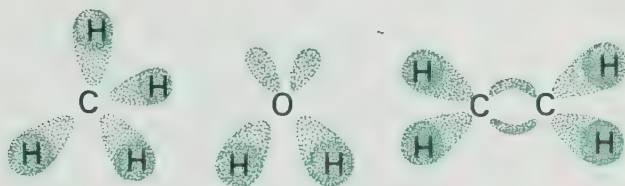


Figure 21. Electron charge clouds for CH_4 , H_2O and C_2H_4

Conclusions

Starting with free atoms and ions, we have constructed valence formulas for many types of molecular systems. We have given much attention to the Lewis theory of valence, indicating how atoms of many elements may achieve stable noble gas configurations in molecules by either electron sharing or electron transfer.

Sometimes, resonance between two or more Lewis structures is needed to describe the electronic structures of certain molecules. If we use Linnett structures with electron-pair bonds and one-electron bonds, we may often dispense with resonance.

We discussed a number of molecules—in particular O_2 —for which Lewis formulas do not account satisfactorily for certain

molecular properties, and we have shown how to improve Lewis formulas by delocalizing lone-pair electrons, thereby generating 'increased-valence' formulas (see Appendix II).

In this booklet, we have said nothing about the thousands of transition metal compounds. A study of these often requires further consideration of the co-ordinate bond and *d* atomic orbitals.

For more than 50 years, the Lewis theory has been used very extensively, and it will continue to be used for many years to come. But I think it is very interesting to see how the theory may be modified and improved. Linnett has demonstrated that one-electron bonds may be used much more extensively than was



Figure 22. Ronald Drayton Brown is Professor and Chairman of the Chemistry Department at Monash University, Victoria. A Fellow of the Australian Academy of Science, Professor Brown's research work has been mainly in the fields of theoretical chemistry and spectroscopy; he has made substantial and pioneering contributions to theoretical chemistry. Educated at Wesley College, Melbourne, he was an undergraduate at the University of Melbourne, then worked at King's College, London, and the University College, London.

realized before 1960. The Ruedenberg theory provides a new understanding of *how* electron sharing produces bonding.

We have introduced briefly the concept of a molecular orbital and its associated electron charge cloud. Molecular orbitals are used very extensively in more advanced descriptions of chemical bonding. Mulliken, about whom we have written on page 21, was one of the outstanding pioneers in the development of molecular orbital theory. The Swedish theoretical chemist P. O. Löwdin, and the French theoretical chemist B. Pullman have stated that one rule of quantum chemistry is 'M.O. = Molecular Orbitals = Mulliken Orbitals', thereby emphasizing the importance of Mulliken's contributions. In Australia, molecular orbital studies of molecules are made at most Universities—in particular by Professor R. D. Brown, at Monash University and Professors D. P. Craig and I. G. Ross and their co-workers, at the Australian National University.

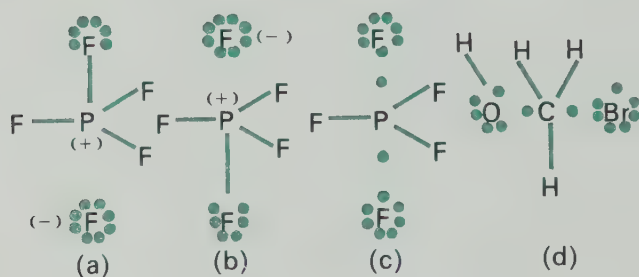
Molecular orbitals are calculated from a quantum mechanical equation which is called the *Schrödinger* equation. This equation can be solved exactly only for a few very simple molecular systems, such as H_2^+ . To obtain good approximate solutions for larger molecules and ions, it is necessary to use electronic computers. In the *Scientific American* April 1970, the American chemist A. C. Wahl, describes the use of computers for this purpose.

Appendix I

PF₅ Reconsidered without using Phosphorus 3d Orbitals

It is also possible to describe the bonding for PF₅, SF₆, ClF₅, and the related systems which we have indicated on pages 32-34 without using the 3d orbitals of the phosphorus, sulphur and chlorine atoms. To demonstrate the procedure, we shall redescribe the bonding of PF₅.

For PF₅, we may assume that the structure of the molecule is represented as PF₄⁺ + F⁻, in which P⁺ is tetravalent in PF₄⁺, just as N⁺ is tetravalent in NH₄⁺. We can then write two Lewis valence formulas for PF₅, namely (a) and (b), in which we have indicated all valence electrons on the two axial fluorines.



We might expect that the bonding between PF₄⁺ + F⁻ is ionic in nature (i.e. it arises from electrostatic attraction between PF₄⁺ and F⁻.) But this is not so, because (a) and (b) are equally acceptable valence formulas for the molecule. We have no way of preferring one formula to the other. Therefore, it seems that we need to use both of them simultaneously to describe the bonding. We have learnt that when we mix two valence structures, i.e. use both structures simultaneously, we speak of **resonance** between the two structures. The resonance between (a) and (b) seems to indicate that the two axial bonds have one electron associated with each of them. To show this very simply Linnett in 1961 and the American chemist G. B. Carpenter in 1963 have implied that we may use valence formula (c). If we use (c) then we no longer need to introduce the concept of resonance or mixing of structures.

If we use either (a) + (b) or (c), we would be led to conclude that the two axial bonds of PF_5 are longer than the three equatorial bonds. Experimental measurements show that this is the case. The three equatorial bonds have lengths of 153.4 pm which are shorter than the two axial bonds with lengths of 157.7 pm.

At present, many research workers are attempting to find out which of the two descriptions of PF_5 and other systems is more satisfactory i.e. whether 3d orbitals of phosphorus participate appreciably in bonding or not. By using quantum mechanical procedures, Professor D. P. Craig and his co-workers at the Australian National University, are investigating this problem.

If *d* orbitals are not needed to bond more than four atoms to another atom, why have molecules such as NF_5 and OF_6 not been reported? Some workers feel that this is because nitrogen and oxygen atoms are smaller than sulphur and phosphorus atoms. Therefore, it is more difficult to arrange five or more atoms around the smaller atoms—there is ‘not enough room’ for them. However, in some chemical reactions carbon atoms are bonded to five atoms in the transition state, the structure of which might be (d) for the reaction of OH^- with CH_3Br in aqueous alkali.

Exercise

23 Without using sulphur or chlorine 3d orbitals, write down valence formulas for the following pairs of molecules:

(i) SF_6 and SF_4 and

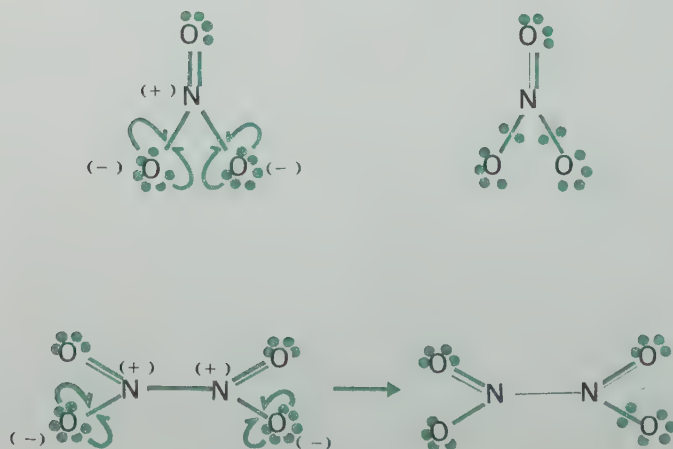
(ii) ClF_5 and ClF_3 .

Appendix II

Increased-Valence Formulas

For many molecules and ions which involve N^+ in the Lewis valence formulas, the measured bond lengths are not compatible with those which are implied by these valence formulas. For example, the nitrogen-oxygen bond length in the nitrate ion NO_3^- , is 123 pm, and the nitrogen-oxygen bond length in dinitrogen tetroxide N_2O_4 , is 118 pm. Both these bond lengths are similar to the bond length of 121 pm for the nitrogen-oxygen double bond of HNO . The Lewis valence formula for N_2O_4 has two nitrogen-oxygen double bonds and two nitrogen-oxygen single bonds. Resonance within this molecule gives four nitrogen-oxygen bonds which are intermediate in length between single and double bonds, and cannot account for the nitrogen-oxygen bonds of N_2O_4 being slightly shorter than the nitrogen-oxygen double bond.

Recently, the author has shown how to improve agreement between theory and experiment. He has demonstrated that it is permissible to move or *delocalize* one or more lone-pair electrons away from atoms carrying charges towards atoms carrying positive charges. The delocalized electrons are positioned in the bond region, as we shall show in the figure. For example, starting with the Lewis valence formulas for NO_3^- and N_2O_4 , we may generate valence formulas which indicate extra NO bonding.



(Electrons have been delocalized from the O^- entities into the NO bond regions, and we have used arrows () to indicate the delocalizations.)

These new valence formulas are called ‘increased valence’ formulas, because more electrons participate in bonding than in the Lewis formulas. In an increased valence formula, a ‘thin’ bond line indicates incomplete sharing of the electron pair by the two bonded atoms. When this occurs, the bond is longer and weaker than a normal electron-pair bond. Can you suggest why the increased-valence formula for N_2O_4 gives a satisfactory account of the NN bond properties?

We may use other procedures to construct increased-valence formulas. For example, if we write down the valence formulas for two nitric oxide molecules and pair together the partial unpaired electron charge on the two nitrogen atoms, we may obtain an increased valence formula for dinitrogen dioxide. This molecule is very unstable, and dissociates into the nitric oxide monomers. The increased valence formula is compatible with this observation, because it indicates that the NN bond should be long and weak. Is the Lewis formula satisfactory with respect to the NN bond?



The increased-valence theory can be applied to thousands of molecules and ions whose Lewis formulas have lone-pairs of electrons.

Exercise

24 Deduce increased-valence formulas for O_3 and HNO_3 .

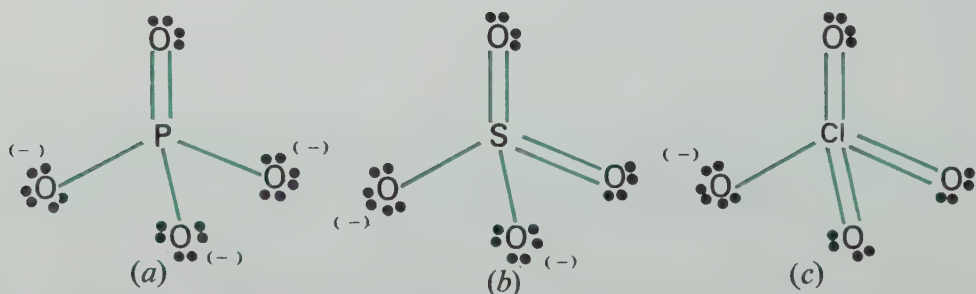
Appendix III

The Phosphate, Sulphate and Perchlorate Anions

The phosphate, sulphate and perchlorate anions, PO_4^{3-} , SO_4^{2-} and ClO_4^- , are tetrahedral anions with four PO, SO or ClO bonds of equal length. The simplest procedure that may be used to obtain valence formulas is to write down valence formulas for the atoms and monatomic ions, and then to pair together the unpaired electrons. Thus from



we may obtain valence formulas (a), (b) and (c), in which the valencies of the phosphorus, sulphur and chlorine atoms are 5, 6 and 7. On page 33, we have found that such valencies can occur if we assume $3d$ as well as $3s$ atomic orbitals may be used for bonding by these atoms.



It should be fairly obvious that for each of (a), (b) and (c), other valence formulas may be written down which differ only in the positions of the double bonds. Resonance between each set of valence formulas can account for the observed equality of the four bond lengths, and also for the regular tetrahedral shapes.

Reading List

Two books which describe the history of valence theory:

Lagowski, J. J. *The Chemical Bond*. Houghton, Mifflin Co., 1966.

Palmer, W. G. *A History of the Concept of Valency to 1930*, Cambridge University Press, 1965.

These books have been used as sources of historical information.

Much of the material which is described in this booklet is also dealt with in the following books. The first three of these do not make much reference to one-electron bonds, and use electrostatics to account for the stability of H_2 . (In this booklet, we have given the quantum mechanical theory of Ruedenberg, which differs from the electrostatic theory.)

Stranks, D. R. et al. *Chemistry A Structural View*, Melbourne University Press, 1970. Chapters 7, 8 and 9.

CHEM Study, *Chemistry—An Experimental Science*. W. H. Freeman and Co., 1967.

Gray, H. B. and Haight, G. P. *Basic Principles of Chemistry*, W. A. Benjamin, 1967, Chapter 11.

Brown, R. D. *Atomic Structure and Valency*, Jacaranda 1966, Chapters 3 and 4.

Lewis, G. N. *Valence and the Structure of Atoms and Molecules*. The Chemical Catalog Co., 1923. Reprinted in 1966 by Dover Publications. This book gives an account of valence theory in the year 1923.

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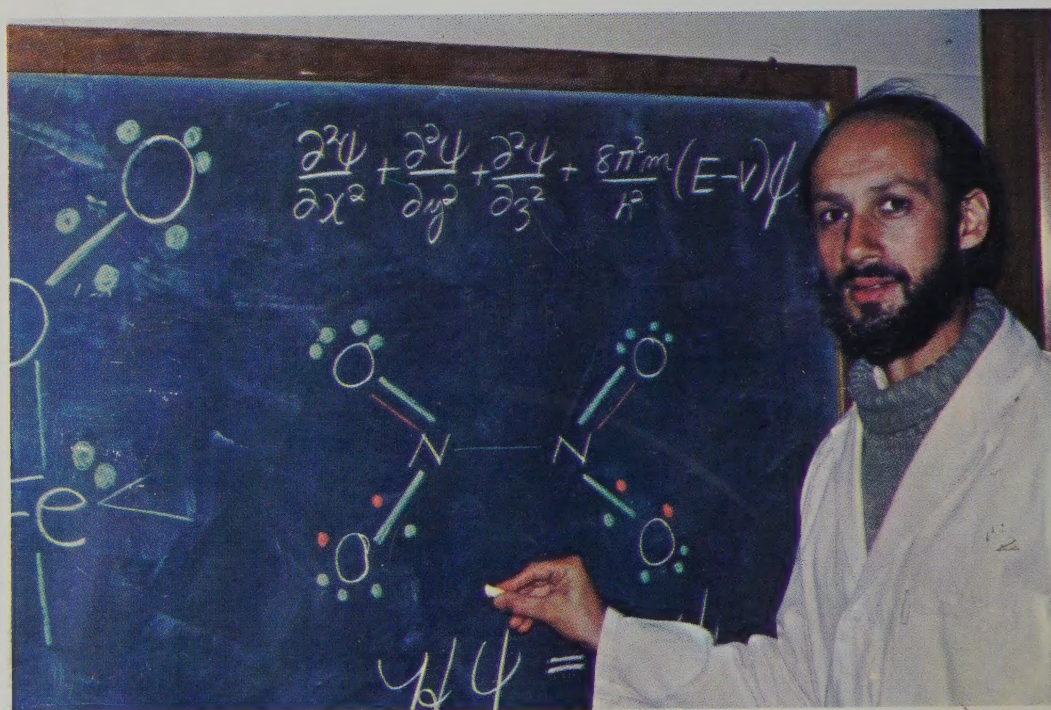
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Dick Harcourt M.Sc., Ph.D., Dip. Ed.

Richard Harcourt, who was educated in Melbourne, has taught with the Victorian Education Department and is now a senior lecturer in physical chemistry at the University of Melbourne. After completing his M.Sc. at Melbourne, he transferred to Monash University, where, working under the direction of Professor R. D. Brown, he gained his Ph.D. degree in 1963. His thesis was based on molecular orbital studies of dinitrogen tetroxide, with a view to explaining the ease of dissociation of this molecule into two nitrogen dioxide molecules. His current interest in valence formulas represents a development of some ideas generated by his doctoral studies. In 1969-70, Dr Harcourt worked in Sweden and Paris, at research institutes. Married, with one child, his interests include cross-country running, and chemistry.

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